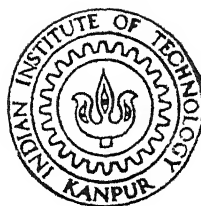# Grafting of Vinyl Monomers Onto Poly (Vinyl Alcohol) Using Poly (Vinyl Alcohol) Copper (II) Complex Initiator

By

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Grafting of vinyl monomers onto poly(vinyl alcohol) using poly(vinyl alcohol) copper(II) complex initiator.

A Thesis submitted
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BY
ADITYA JOSHI

TO

THE DEPARTMENT OF CHEMICAL ENGINEERING

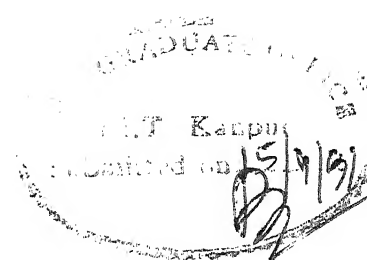**INDIAN INSTITUTE OF TECHNOLOGY**

KANPUR-208016

APRIL 1991

CERTIFICATE

This is to certify that the work titled 'Grafting of Vinyl Monomers onto Poly(vinyl Alcohol) Using PVA-Cu(II) Comple Initiator' has been carried out by Mr. Aditya Joshi under supervision and that this work has not been presented elsewhe for a degree.

April 15, 1991

ANIL KUMAR
Professor
Department of Chemical Engineering
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Kanpur - 208016

Dedicated to my parents

ACKNOWLEDGEMENTS

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NOTATIONS

V : Volume fraction of aqueous phase

OH_c : PVA-Cu(II) complex

$R_G\cdot$: Graft polymer radical produced on PVA chain

$\cdot CCl_3$: Trichloromethyl radical

$R_G P_n$: Graft polymer radical

P_n : Homopolymer radical

M : Monomer

$R_G M_n$: Dead graft copolymer

M_n : Dead homopolymer

K : Rate constant

λ_k : kth moment where ($k = 0,1$ and 2)

c : Concentrations

η : Viscosity

t : Drain time

η_{rel} : Relative viscosity

η_{sp} : Specific viscosity

η_r : Reduced viscosity (dl/gm)

η_{inh} : Inherent viscosity

$[\eta]$: Intrinsic viscosity (dl/gm)

$\bar{M}_v$: Viscosity average molecular weight

Superscript w : Water (aqueous) phase

Superscript d : Droplet phase

Subscript s : Solvent

ABSTRACT

The formations of grafts of methyl methacrylate and styrene onto Poly(vinyl alcohol) backbone in the presence of carbon tetrachloride (CCl_4) has been studied using PVA Cu(II) complex as initiator. The polymerization reaction mass is heterogeneous in nature and leads to the formation of both graft copolymer and homopolymer. It has been found that the amount of graft copolymer formed increases with time whereas the amount of homopolymer first increases with time and after a certain time decreases giving predominantly graft copolymer at longer times. It has been found that reaction temperature, initial pH of the complex, amount of CCl_4 and PVA concentration are important parameters which affect the polymerization reaction. Their effect on the reaction rate has been studied. A theoretical kinetic model has been proposed which accounts for the heterogeneity of the system. The governing mole balance equations and the moment equations for the various molecular and intermediate species have been derived and solved numerically.

CHAPTER 1

INTRODUCTION

A copolymer is formed by incorporating two or more different monomers in the same polymer chain. These different monomers are known as comonomers. The formation of a copolymer may be represented as

$$A + B \longrightarrow (- A - B -)_n$$
$$\text{(comonomers)} \qquad \text{(copolymer)}$$
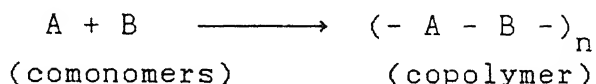
With copolymers one can achieve combinations of material properties such as tensile strength, solvent resistance, low temperature flexibility which cannot be obtained with individual homopolymers[1]. Consequently, research interest has shifted towards synthesizing such multicomponent polymer systems in order to develop certain desirable properties in them.

Copolymers may be classified on the basis of distribution of monomer units within the copolymer molecule. Accordingly, monomer units placed in a random manner within the molecule results in a random copolymer. They may be represented as ABBABABAAB where A and B are the monomer units. Many random copolymers find applications as elastomers and plastics. Examples of this type are SBR, NBR (polybutadiene-co-acrylonitrile).

An alternating copolymer is one in which the monomer units are arranged alternately. They are represented as ABABABABAB. A commercial example of this type of copolymer is Poly(styrene-alt-maleic anhydride). These copolymer resins[1]

are used as reactive additives[1] for latex paints, pigment dispersants, floor polishes etc.

In block copolymers, there is a long chain or block of one monomer followed by a block of another monomer i.e., AAAAAABBBBBBBB. Industrially, it is important because of its unique structure property relationships and has applications as thermoplastic elastomers (having hard glassy or crystalline blocks and soft elastomeric or rubbery blocks), elastomeric fibres (hard urethane blocks with soft polyester blocks), toughened thermoplastic resins and surfactants.

A graft copolymer is formed by introducing branches of one polymer onto the backbone of another polymer. Structurally it may be represented as:

$$A \quad A \quad A \quad A \quad A \quad A \quad A$$
$$B$$
$$B$$
$$B$$
$$B$$
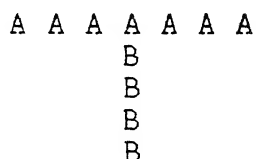
where A represents the backbone polymer and B represents the branches. Two commercially significant graft copolymers are ABS (acrylonitrile-butadiene styrene) resins and IPS (impact polystyrene) plastics.

ABS and IPS find applications where high tensile strength, rigidity, resistance to brittle fracture stability at high temperatures are required. Also, because of one dissimiliarities in physical properties of the branches constituting the graft copolymer, they commonly are used as emulsifiers, surfactants, surface modifiers and compatibilizers in blends. Free radical copolymerizations can be carried out in bulk (comonomers without

solvent) in solution (with solvent), in suspension (monomer droplets suspended in a medium such as water) and in emulsion (droplets emulsified in water).

The object of our experimental work has been to study the grafting of poly(methyl methacrylate) (PMMA) and polystyrene onto poly(vinyl alcohol). PVA is an important engineering material. A few of its applications which are worth mentioning[2] are 1) as adhesives 2) as emulsion stabilizers 3) in textile warp sizes for cotton and staple yarns and 4) in paper making. Poly(vinyl alcohol) (PVA) is a water soluble material. Introducing hydrophobic chains of PMMA or polystyrene onto the hydrophilic PVA backbone would introduce moisture resistant properties in the resulting copolymer. It is also used as an emulsifier because of the hydrophilic hydrophobic character in the molecule.

A considerable work has been directed towards grafting of PVA[3,4] in which grafts of acrylamide, acrylonitrile, vinyl acetate and methyl acrylate were generated using ceric salts i.e. ceric ammonium nitrate. In this reaction, poly (vinyl alcohol) acts as a reducing agent and the ceric ion acts as an oxidising agent resulting in the formation of a free radical on the polymeric backbone. This free radical in the presence of vinyl monomer then initiates polymerization resulting in substantially pure graft copolymer.

Ikada et al.[5] conducted the graft copolymerization of methyl methacrylate (MMA) onto PVA using potassium persulphate (KPS) as initiator in aqueous and dimethyl sulfoxide (DMSO) media. The copolymerization was carried out in three different

ways with water swollen PVA film containing KPS and with PVA solutions containing KPS in water and in DMSO.

Interest in recent times has been focussed on the grafting onto natural polymers such as gelatin, starch, casein, guar gum, cellulose and natural fibres such as cotton, silk and also natural rubber. Incentive for all these studies is to introduce desirable properties in these reactions. Raval et al.[6] grafted methyl methacrylate onto guar gum in an aqueous slurry using hydrogen peroxide as initiator. The copolymers were characterized by IR spectroscopy. The effect of H_2O_2 concentration, amount of guar gum and reaction times on grafting parameters such as % grafting, grafting efficiency were studied. Bajpai et al.[7] studied the grafting of acrylamide onto guar gum in aqueous medium initiated by $KMnO_4$/oxalic acid redox system. It was found that the rate of grafting increases with increase in temperature and concentrations of redox components and acrylamide, but decrease at higher concentrations of guar gum. The same findings were reported[8] when potassium persulphate/ascorbic acid redox sys tem was used for the above graft copolymerization.

Okoniewski et al.[9] studied the graft copolymerization of acrylic acid onto poly(ethylene terephthalate) fibres (PET) using benzoyl peroxide initiator. It was found that the grafting yield increases with the increase in monomer concentration, temperature and the concentration of benzoyl peroxide. Samal et al.[10] have studied the graft copolymerization of MMA onto cotton - cellulose using hexavalent chromium Cr(VI) as initiator. The reaction were carried out in an aqeous methanolic solution of perchloric acid.

The % grafting was first found to increase with MMA concentration and then decrease beyond a certain MMA concentration. The same trtend was observed with increasing Cr(VI) concentration perchloric acid concentration and temperature.

Mohan et al.[11,16] studied the graft copolymerization of acrylate monomers onto casein. Butyl acrylate and methyl acrylate were the monomers used in the study and potassium peroxydisulphate ascorbic acid was used as the initiating system. Effects of monomer concentration, initiator concentration, activator concentration, backbone concentration (Casein) and temperature on rate of polymerization, percent grafting and grafting efficiency were studied.

Samal et al.[12] studied the graft copolymerization of MMA onto silk fibres. The reaction was conducted in aqueous solution using acetylacetonate Mn (III) complex and perchloric acid was used as the catalyst. Graft yield was observed to first increase and then decrease beyond a certain MMA Mn(III) and complex concentration and perchloric acid concentration. Methyl methacrylate[13] was also grafted onto rubber using the above complex. Acrylonitrile[14] was successfully grafted onto Hemicellulose using ceric ammonium nitrate as initiator·Proof for grafting was provided through IR analysis.

Stejskal[15] et al. studied the grafting of MMA onto gelatin backbone in aqueous medium. The graft copolymerization resulted in the graft copolymer, ungrafted gelatin and PMMA homopolymer. Water-Methyl ethyl ketone mixture was used to separate these components. A similar technique has been used to effect

separation in our experimental work.

Grafting of methyl methacrylate - methacrylate acid monomer pair onto poly(vinyl chloride) and chlorinated rubber was studied by Sankholkar[17] and Deb. AIBN and n-butane thiol-dimethyl sulfoxide were used as initiators.

Poly(vinyl alcohol) copper (II) complex acts as an initiating system for graft copolymerization with vinyl monomers such as styrene or MMA. The PVA-copper (II) complex[18] is synthesized by addition of copper nitrate (or cupric chloride) solution and a strong base such as NaOH to a dilute aqueous solution of Poly(vinyl alcohol). It has been seen that the complex is formed at pH higher than 5.7. The complex solution r emains stable without precipitation of copper hydroxide even at high pH. The chelate solution becomes deeply green with increasing neutralization (a fact which was also noticed during our work). Godard et al.[18] have proposed a structure for the PVA-copper (II) complex (Fig.1). Two copper ions are joined together by two oxygen bridges. Each copper ion is in turn coordinated to two hydroxyl groups of the PVA chain and several binuclear $(CuO)_2$ group are complexed on the same PVA chain.

Kimura et al.[19] studied the polymerization of acrylonitrile, methyl methacrylate and styrene initiated by copper(II) chelate in the presence of carbon tetrachloride. Polymerization was carried out in sealed tubes in which fixed amount of vinyl monomer and carbon tetrachloride were added to an aqueous copper (II) chelate solution. The degassed and sealed tubes were shaken in an incubator at $60^{\circ}C$ for 3 hours. The

polymer was precipitated in excess methanol and dried for 15 hr in vacuum. The effect of various parameters such as metal-ligand mole ratio ([(CuCl$_2$]/[PVA] ratio), pH of the system, temperature and effect of the degree of polymerization of PVA was studied. It was found that in the polymerization initiated by the copper complex, conversion was found in the order MMA > styrene >> acrylonitrile. It was also found that in th pH range from 5.6 to 8 conversion increases with the rise in the chelate concentration, but in the pH range 8-10, conversion decreases due to precipitation of the chelate and beyond pH 10, conversion shows a drastic increase.

Kimura et al.[20] also studied the initiation mechanism of vinyl polymerization by copper (II) chelate of PVA in the presence of carbon tetrachloride. This was done in order to determine the free radical species formed during the initiation step. The following scheme was proposed

$$Cu(II)(OH-R)_n + R - O^- \longrightarrow Cu(I)(HO-R)_n + R-O. \qquad (i)$$

$$R-O. + CCl_4 \longrightarrow .CCl_3 + ROCl \qquad (ii)$$

$$R-O. \text{ or } .CCl_3 + monomer \longrightarrow monomer radical \qquad (iii)$$
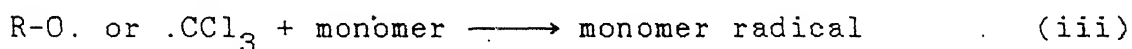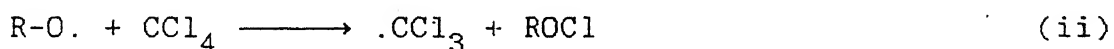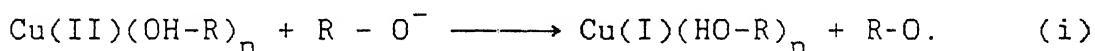
PVA - Copper (II) chelate undergoes a redox reaction with an alkoxide (R-O$^-$) to form the free alkoxy radicals (R-O.). which undergo a transfer reaction with CCl$_4$ to form trichloromethyl radicals (.CCl$_3$). These trichloromethyl radicals along with the alkoxy radicals can initiate the vinyl polymerization .

We have studied the grafting of MMA and styrene onto PVA backbone in the presence of CCl$_4$. PVA copper (II) complex was used as the initiating system to effect copolymerization. Since

the reaction mass consists of two separate species, it is a heterogeneous polymerization reaction system. The technique used for the separation of the components is based on an earlier study[15]. Rate and molecular weight data were obtained. A kinetic model has been proposed to explain the mechanism of grafting. Mole balances and moment equations for the various species involved have also been derived.

CHAPTER 2

EXPERIMENTAL PROCEDURE

Reagents and chemicals used in our experiments were as follows:

1) Polyvinyl (alcohol)(cold PVA) (LR grade, New Modern Chemical Corporation)

2) Methyl methacrylate (LR grade, Robert Johnson)

3) Carbon tetrachloride (LR grade),(Ranbaxy Laboratories Ltd., Punjab-160 051)

4) Copper (II) chloride (LR grade, s.d. Fine-Chem Pvt. Ltd., Boisar)

5) Sodium hydroxide pellets (LR grade, Ranbaxy Laboratories Ltd.)

6) Fused calcium chloride (LR grade, New India Chemical Enterprises)

7) Acetone (LR grade Qualigens Fine Chemicals, Bombay-400 026)

8) Hydroquinone (LR grade, Loba Chemie Indo Austranal Co.)

9) Benzene (LR grade s.d. Fine-Chem Pvt. Ltd.)

10) Methyl ethyl ketone (MEK) (LR grade, Loba Chemie Bombay-400002)

Distilled water produced in the laboratory itself was used in all the experiments.

i) Purification of Methyl Methacrylate Monomer (MMA)

Laboratory grade methyl methacrylate monomer (MMA) comes with traces of hydroquinone inhibitor which was removed as follows.

MMA was washed thrice with N/10 sodium hydroxide solution in a separating funnel. The inhibitor preferentially goes into the aqueous phase which was removed after settling. The MMA was washed once with distilled water to remove the remaining NaOH out of it. The absence of NaOH from MMA was confirmed by Red Litmus paper. After this, fused calcium chloride pellets were added to the MMA to dry it. It was stored in the freezer before use. The procedure for purifying styrene is the same as that for MMA.

ii) Preparation of PVA Copper Complex

A given amount of polyvinyl alcohol (10 gm) was dissolved in 300 cc distilled water with constant stirring by means of a magnetic stirrer. A known quantity of aqueous copper (II) chloride solution (0.1657g $CuCl_2.2H_2O$ in 100 cc water) was then added to it. The mixture was stirred for at least four hours. The PVA complex formation occurs after sodium hydroxide solution is added to this with continuous stirring. The process of complexation is found to get completed in two hours. The pH of the complex was adjusted by adding NaOH solution and the resultant solution was stored overnight at room temperature before being used in the reaction.

iii) Experimental Set-up

The exprimental set-up consisted of a 4 necked glass reactor (Borosil) of 500 ml capacity which was provided with a stirrer. The reactor was immersed in a water bath of 30 litre capacity. The water bath temperature was controlled by means of a temperature controller (Model: Siskin Julabo-V) (Fig.2).

Polymerization Reaction Procedure

The temperature of the bath was maintained at the desired temperature. The reactor was purged with nitrogen gas for 10-15 minutes. A 100 ml of the purified MMA was then poured into the reactor, to which a given quantity of carbon tetrachloride (50 cc) was added. Finally, 250 ml of PVA - Copper (II) complex was introduced to the reactor. The first sample (20 ml) was withdrawn after allowing the reactants to mix completely. Thereafter twenty mililitre samples were withdrawn every half an hour. To each sample were added a few drops of hydroquinone inhibitor. The pH of the samples was measured by a pH meter (Model: Systronics pH meter 335). The products of the samples were precipitated in excess acetone. The samples were then kept overnight at $0^{\circ}C$ to ensure total precipitation. The samples were then dried at $80^{\circ}C$ for 24 hours on preweighed petridishes in an oven and then weighed to yield the weight of the dried polymer. These dried samples were retained for further analysis (For the run using styrene 100 ml of purified styrene was used instead of MMA). The results were expressed in the form of percent increase in polymer weight which is given by the formula:

$$\text{percent increase in polymer weight} = \frac{m_t - m_o}{m_o} \times 100$$

where,

m_o : weight of dried sample at time t=0, gm

m_t : weight of dried sample at any time t, gm

Sample Analysis

The dried samples consist of graft copolymer, homopolymer and ungrafted PVA. The samples were analysed to ascertain the

amounts of these three constituents in it. Equal quantities of distilled water and ethyl methyl ketone (MEK) were added to the sample. The solution was warmed until a macroscopically homogeneous (although turbid) solution was formed. This solution in glass tubes was centrifuged at 10000 rpm for one hour (Model: A dams Analytical centrifuge, 115 volts, 1.5 Amp). Three layers were observed in the glass tubes which were identified to be 1) The upper layer (MEK rich) containing polymethyl methacrylate (PMMA), 2) The lower layer (Water rich) containing ungrafted PVA, and 3) the middle layer containing the graft copolymer. Each of these layers was isolated and dried in the oven on separate preweighed pertridishes and weighed to yield the weights of the three constituents.

Hydrolysis of PVA Backbone[21]

The graft copolymer was treated with acidified potassium dichromate solution for about 4 hours in order to hydrolyse the PVA backbone. Independant experiments with PVA have shown that this is sufficient for the complete hydrolysis of the PVA. It has also been seen that PMMA is unaffected by this treatment. The solution was filtered and the PMMA collected washed with water and dried in the oven. This PMMA was then used in the determination of viscosity average molecular weights ($\overline{M}_v$).

The same method can be used for degrading the PVA backbone of the PVA – polystyrene graft copolymer with the polystyrene branches remaining unaffected.

Determination of Viscosity Average Molecular Weights ($\overline{M}_v$)

The viscosity average molecular weights of the homopolymer

and the PMMA branches obtained by hydrolysing the PVA backbone of the graft copolymer was determined by using a Cannon viscometer (75 ml, S189). The same procedure was employed for the polystyrene homopolymer and polystyrene branches obtained from the graft copolymer.

A known quantity of the PMMA was dissolved in 15 ml benzene and this solution was taken in one bulb of the viscomet er. The drain times for each of the four bulbs was determined using a stop watch and the average time (t) was computed. 5 ml of pure benzene was then added to the bulb of the viscometer and the above procedure was repeated. This procedure was carried out for four such dilutions. Readings were also taken for pure benzene to yield the drain time for pure solvent (t_s). A table of concentrations of PMMA in benzene (c) and average drain time (t) was obtained from which the viscosity average molecular weight ($\overline{M}_v$) was calculated as follows:

For the Cannon viscometer we know that

$$\frac{\eta}{\eta_s} = \frac{t}{t_s} \qquad (i)$$

where, η, η_s are the viscosities of solution and pure solvent respectively and t, t_s are the corresponding drain times of solution and solvent respectively.

The terms used in viscometry are:

Relative viscosity: $\eta_{rel} = \eta/\eta_s$ $\qquad$ (ii)

Specific viscosity: $\eta_{sp} = \left(\frac{\eta}{\eta_s} - 1\right) = \eta_{rel} - 1$ $\qquad$ (iii)

Reduced viscosity : $\eta_r = \eta_{sp}/C$ (units dl/gm) $\qquad$ (iv)

where c is the concentration of the polymer in the solution (g/dl).

Inherent viscosity: $\eta_{inh} = \dfrac{\ln \eta_r}{c}$ (v)

Intrinsic viscosity: $[\eta] = \dfrac{\eta_{sp}}{C} = \dfrac{\ln \eta_r}{C}$ (units dl/gm)

$\qquad\qquad\qquad\qquad (C \to 0)\ (C \to 0)$

From the viscometer readings, we have a table of concentrations, C(g/dl) and the corresponding average drain time, t (sec). For each concentration the quantities as given by eqns. (i) to (v) are computed and a double extrapolation plot of η_r and η_{inh} versus concentration C(g/dl) (both extrapolated to zero concentration) is prepared. The common ordinate on the viscosity axis gives the intrinsic viscosity [η].

The viscosity average molecular weight can then be computed from the Mark Houwink equation:

$$[\eta] = K \overline{M}_v^{\,a}$$

where, K(dl/gm) and a are the Mark Houwink constants which can be obtained from the Polymer Handbook[22].

For solutions of polymethyl methacrylate in benzene at 30°C, the following equation was used

$$[\eta] = 5.2 \times 10^{-5}\ \overline{M}_v^{0.76}$$

where [η] is in dl/gm, (applicable in the molecular weight range $6 \times 10^4 - 250 \times 10^4$).

For solutions of polystyrene in benzene at 25°C, the following equation was used to compute the molecular weights of polystyrene homopolymer and polystyrene grafts

$$[\eta] = 12.3 \times 10^{-5}\ \overline{M}_v^{0.72}$$

where [η] is in dl/gm (applicable in the molecular weight range $0.6 \times 10^4 - 520 \times 10^4$)

For solutions of polyvinyl alcohol in water at $25^{\circ}C$, the following equation was used

$$[\eta] = 300 \times 10^{-5} \, \bar{M}_v^{0.5}$$

where $[\eta]$ is in dl/gm (applicable in the molecular weight range 0.9×10^4 - 17×10^4). This was used for characterizing the PVA. The viscosity average molecular weight ($\bar{M}_v$) for PVA used in the experiments was found out to be 53,200.

CHAPTER 3

DESCRIPTION OF THE MODEL

The reaction under study is conducted by stirring a known quantity of PVA-Cu(II) complex with MMA (or styrene) and CCl_4 at a fixed temperature. Due to the low solubility of MMA (or styrene) and CCl_4 in water and of PVA in MMA (or styrene) and CCl_4, the reaction mass may be considered to be made of two separate phases: the aqueous phase in which MMA and CCl_4 are dispersed in the form of droplets which constitute the second phase viz the droplet phase. PVA being highly soluble in water, may be considered to remain entirely in the aqueous phse. The aqueous phase, initially consists of PVA - Cu(II) complex in chemical equilibrium with PVA and $CuCl_2$ while the droplet phase consists of MMA (or styrene) and CCl_4.

Since the reaction mass comprises of two phases, it is a heterogeneous reaction system. So, as with all heterogeneous systems, two steps namely interphase diffusion of components followed by reaction are involved. Since the reactions take place in both the phases, mole balances for the different species have to be made separately for each phase. Due to the concentration gradient, CCl_4 diffuses from the droplet phase to the aqueous phase. In the aqueous phase, CCl_4 is involved in an initiation step with the PVA-Cu(II) complex leading to the formation of trichloromethyl radicals ($.CCl_3$) and free radicals on the PVA backbone ($R_G.$) Monomer (M) also diffuses from the droplet to the aqueous phase due to the concentration gradient.

In the aqueous phase the free radicals, $.CCl_3$ and $R_G.$ interact with the monomer to give rise to the homopolymer (P_1) and graft copolymer radicals (R_GP_1) respectively. Similarly, in the droplet phase CCl_3 radicals (generated in the chain transfer reactions) give rise to homopolymer radicals (P_1). Since there would no complex in the droplet phase, $R_G.$ cannot be formed on the droplet, so there would not be any generation of graft copolymer radicals in the droplet phase.

In the both the phases, the homopolymer and graft copolymer radicals undergo propagation reactions with the monomer leading to an increase in chain length. Both the radicals $(R_GP_n$ and $P_n)$ can undergo interphase diffusion (from aqueous phase to droplet phase).

As with all addition polymerizations, termination can take place in two ways i.e. combination and disproportionation. Termination (in both phases) of a growing graft copolymer chain can take place by another growing graft copolymer chain or by a growing homopolymer chain. A growing homopolymer chain can also be terminated by another homopolymer radical. Termination by combination however, of one graft copolymer chain by another in both the phases is less likely to occur and hence has not been considered in the model.

Chain transfer can take place with CCl_4, with monomer and with dead polymer. Chain transfer leads to the formation of more chains of shorter chain lengths (and hence low molecular weights): Chain transfer with CCl_4 leads to the generation of trichloromethyl radicals which would leads to the generation of

more polymer radicals. Chain transfer with monomer leads to the formation of dead polymer and generation of homopolymer radicals. Chain transfer with dead polymer can take place with both dead graft copolymer as well as with dead homopolymer. Chain transfer reaction of a graft copolymer radical with a dead graft copolymer molecule would occur with less likelihood and hence has not been considered in the model.

As the reaction proceeds, the monomer and PVA concentration decrease and the dead polymer concentration increases. Both the dead polymer species can also undergo interphase diffusion. The schematic representation of the model has been shown in Fig.3. In writing the mole balances for the species two assumptions have been made 1) Radicals once adsorbed on the droplet stay there and 2) One could assume the monomer and polymer species as one phase of constant volume. Mole balances have been made for CCl_4 monomer and PVA. Moment equations (Zeroth, first and second moments) have been written for the dead polymer species from which we obtain seventeen ordinary differential equations (ODEs). Balance equations have been written for the intermediate species (.CCl_3, R_G., R_GP_n and P_n). According to the steady state hypothesis, the rate of change of intermediates is zero and hence we get a set of fifteen algebraic equations. The mole balances for the various species have been presented in Table 3. The moment equations have been presented in Table 4. The algebraic equations have been shown in Table 5. A sample derivation of moment equations for a dead polymer species from the general mole balance has been shown in Table 7.

CHAPTER 4

COMPUTATIONAL SCHEME

Mole balances on the three species CCl_4, monomer and PVA, along with the moment equations for the dead polymer species yield seventeen ordinary differential equations (Equations 1-17). These are in Tables 3 and 4 respectively. Similarly, a balance on each of the intermediate radical species (along with t he moment equations) give fifteen algebraic equations (Equations I - XV). These are given in Table 5.

At the beginning of the program, the initial values of concentrations of the species CCl_4, monomer, (M) PVA (as used in the experiments) and the rate constants are fed into the computer. The moments of the dead polymer species $(\lambda_0, \lambda_1, \lambda_2)$ are set equal to zero and the guess values are given to $\lambda_{P^w_{no}}$ and $\lambda_{R_G P^d_{no}}$. At every time interval, the moments of the intermediate species $(P_n, R_G P_n)$ and concentrations of $.CCl_3$ and $R_G.$ are computed by solving equations I-XV. These values are then made use of in order to numerically differentiate equations 1 to 17 using the Runge Kutta fourth order technique.

The program structure comprises of three parts 1) Main Program 2) Subroutine Radical and 3) Subroutine Newton. The first step is to call subroutine Radical from the main program which in turn calls subroutine Newton. In subroutine Nwton, equations (IV), (VII), (X), (XII) are solved using the Newton

Raphson iterative technique. Using the guess values of $\lambda_{P_{no}}w$ and $\lambda_{R_GP_{no}}d$ and the other values from the previous time interval, quadratic equation (IV) is solved and positive root selected to yield the value of $\lambda_{P_{no}}d$. Following this, quadratic Equation (XIII) is solved from which the value of $\lambda_{R_GP_{no}}w$ is obtained. These values are then used in equation (X) (function of $\lambda_{P_{no}}w$) and equation (XIII) (function of $\lambda_{R_GP_{no}}d$) and the various derivatives evaluated. New values of $\lambda_{P_{no}}w$ and $\lambda_{R_GP_{no}}d$ are then obtained using the Newton Raphson iterative technique. If the percent change from the value in the previous iteration is less than a specified tolerance value (EPS in the program), then the converged values of $\lambda_{P_{no}}w$, $\lambda_{R_GP_{no}}d$, $\lambda_{P_{no}}d$, $\lambda_{R_GP_{no}}w$ are returned to the subroutine Radical. Otherwise computation is continued as before in the subroutine Newton till convergence is attained. The various equations used in subroutine Newton have been presented in Table 6. Values of $\lambda_{P_{no}}w$ and $\lambda_{R_GP_{no}}d$ obtained in the preceding time interval are used as guess values in the next time interval.

In subroutine Radical, the first moment Equations (V), (VIII), (XI) and (XIV) and second moment Equations (VI), (IX), (XII), (XV) are solved mutually exclusive by using Cramer's rule. The $.CCl_3$ concentration in both phases is then calculated using Equations (II) and (III). These values are then used in the main program along the various molecular species concentrations (PVA, M, CCl_4) and moments (R_GM_n and M_n) and their values in the next time interval computed by using the Runge Kutta fourth order

technique.

Time increment (Δt) used in the program was 90 seconds and computation was carried out for a reaction time of four hours. This time increment was chosen after making a stability analysis of the program. Computation was carried out by choosing different time intervals viz. 200 secs, 160 secs, 120 secs, 90 secs, 60 secs and 20 seconds. It was found by comparing the outputs that a Δt of 90 seconds was the highest Δt at which a stable solution was obtained. Hence a Δt of 90 seconds was chosen.

CHAPTER 5

RESULTS AND DISCUSSION

The reaction was conducted by stirring together, PVA copper (II) complex, CCl_4 and the monomer in a reactor. Samples were withdrawn at regular time intervals; their pH was measured and then the polymer formed was dried after precipitation with acetone. The dry weights were recorded (expressed as percent increase in weight in Figs. 15-18. Then the grafted material, homopolymer and ungrafted PVA were separated from each other using the technique described earlier. Finally, the molecular weights of the homopolymer and graft copolymer were determined using the viscometric technique. In all runs (conducted with both methyl methacrylate and styrene) the pH was obtained to decrease as the polymerization progressed (ref to Fig.4 and Figs. 11-14). In the initiation step when the PVA copper (II) complex interacts with CCl_4, hydrogen ions are generated leading to the decrease in pH observed. Furthermore, the weight of the dried samples was found to increase with time (ref. to Fig 5 and Figs. 15-18. As the reaction proceeds, the PVA complex and monomer get consumed and graft copolymer and homopolymer are formed, thus the solid content of the reaction mass increases with time. This explains the above observation regarding the increase in dried weight with time.

In three of the runs, two with methyl methacrylate and one

with styrene, the ungrafted PVA component of the mixture graft copolymer and the homopolymer were separated and their weights plotted as a function of time (Fig.6-8). As expected, the amount of ungrafted PVA was found to decrease with time. It was also seen that the amount of graft copolymer formed increases with time. With one run conducted with MMA (pH of the complex = 9.26, Temp. =70) and as seen from Fig.6 and with styrene (Fig.8) amount of homopolymer formed first increases with time and after a certain time, it was found to decrease with time. The similar trend was however, not observed (Fig.7) in the run carried out using MMA and PVA complex of pH 10.1 at a temperature of $80^{\circ}C$ in the time for which the reaction was carried out. It may well be that at higher temperature and higher pH of the complex, it takes a longer time for the homopolymer amount to attain a maxima and then decrease. Also upon comparing Fig.6 and Fig. 7 it is also seen that the relative amounts of graft copolymer and homopolymer formed increases with increase in temperature and pH of the complex. It would also mean that at larger times, the formation of homopolymer is suppressed and we would get predominantly graft copolymer. Molecular weights of homopolymer and of the branches obttained after degradation of the PVA backbone have been shown in Figs. 9 and 10. It is seen that the homopolymer molecular weight levels off after a certain time (in the case of both styrene and methyl methacrylate). It is also observed that the molecular weight of the grafts of PMMA and polystyrene increases with time. In all the cases the molecular weight of the PMMA (or polystyrene grafts was more than that of the homopolymer.

Run were taken in order to investigate the effect of the parameters 1) Reaction temperature 2) Initial pH of the complex 3) PVA concentration and 4) Amount of CCl_4 on the polymerization reaction. In these runs, one of the parameters was varied with the other three maintained constant. The pH and percent increase in weight (dried weight) were plotted against time.

Effect of Temperature

The effect of temperature was investigated by conducting runs at three different temperatures i.e. $60^{\circ}C$, $70^{\circ}C$ and $80^{\circ}C$ (maintaining the other three above mentioned parameters consotant for these runs). Fig.11 shows the variation of pH of the reaction mass with time for these three temperatures. It is seen that at any given time, the pH decreases faster with increase in temperature. Fig.15 shows the percent change in dried weight against time. At $80^{\circ}C$, there is an exceptionally large increase in weight (around 900% increase) as compared to the maximum increase of around 300% at $70^{\circ}C$ and a maximum increase of around 75% at $60^{\circ}C$. Both Figs. 11 and 15, thus indicate that the rate of polymerization increases with increase in temperature. At higher temperature, viscosity of the reaction mass decreases and the diffusion coefficients and kinetic rate constants would increase. Consequently the rate of polymerization would be high at higher temperature. Also, as seen from Figs. 6 and 7, extent of grafting is more at higher temperature.

Effect of the Initial pH of the Complex

Effect of this parameter was investigated by conducting runs using PVA copper (II) complex of three different initial pH

(8.02, 9.26 and 10.17) keeping the other parameters constant. All runs were conducted at 70°C. It was found that the effect of the initial pH of the complex was not unlike that of temperature. As is seen from Fig.12, at a given time, the pH of the reaction mass decreases more rapidly with increase in the pH of the complex. Similarly observations were made with the percent increase in the polymer weight with time (Fig.16). It would mean that the rate increases with the increase in the pH of the PVA complex used. In fact, there is a sharp increase in polymer weight in case of complex pH=10.17 (about 300% after 4 hours). At higher pH, extent of complexation of PVA is more; so there is a higher concentration of the PVA complex in the reaction mass. Hence the rate is higher at higher pH. Also, from figure 7 it is seen that at higher temperature and higher pH of the complex, there is a high yield of the graft copolymer. The higher rate and high PVA complex concentration at these conditions leads to more radicals on the PVA backbone and hence leads to the formation of more graft copolymer.

Effect of PVA Concentration

In this the amount of PVA used during the preparation of the complex was varied. Three runs were taken at 70°C using PVA complex solutions of pH around 10.2±0.1 which were prepared by using 5 gm, 10 gm, and 15 gm of PVA respectively. From figures 13 and 17, it is seen that at a gives time the rate of polymerization increases with increase in amount of PVA from 5g to 10 gm but beyond 10 gm of PVA, the rate decreases (as is seen from the curve for 15 gm PVA). From figure 17 it is also seen

that with 10 gm PVA, there is a phenomenally increase in polymer weight as compared to the curves for 5g and 15 g PVA.

Effect of Amount of CCl_4

In this set, the amount of CCl_4 used was varied keeping the other parameters constant. Four runs were conducted in this manner at $70^{\circ}C$ with complex of pH round 10.1 ± 0.1 and by varying the amount of CCl_4 (0 cc CCl_4, 25 cc CCl_4, 50 cc CCl_4, 65 cc CCl_4). The variation in pH and percent increase in weight are plotted against time in figures 14 and 18 respectively. From the pH change and extent of change in weight of the polymer, it is seen that there is negligible polymerization in the absence of CCl_4. This is so because CCl_4 is necessary in the initiation step for the generation of trichloromethyl and graft copolymer radicals which in turn would give rise to homopolymer and graft copolymer chains. Also, at a given time, the rate and extent of polymerization increases with increase in amount of CCl_4 (upto 50 cc CCl_4). Beyong 50cc CCl_4 (as seen from the curve for 65 cc CCl_4 in Figures 14 and 18) at a given time the rate of polymerization decreases with increase in CCl_4.

CHAPTER 6

CONCLUSIONS

In this work, we have studied the graft copolymerization of methyl methacrylate (MMA) and styrene onto poly(vinyl alcohol) backbone. Using the set of conditions (as described in experimental procedure) we have succeeded in forming grafts of poly (methyl methacrylate) and polystyrene onto poly(vinyl alcohol). We have also separated ungrafted PVA, homopolymer and graft copolymer using the technique described earlier. We have seen that the amount of graft copolymer formed increases with time whereas the homopolymer first increases with time and after a certain time, the homopolymer amount drops. Thus, at longer times, we would get predominantly graft copolymer. This trend was observed in the case of both MMA and styrene. Amount of graft copolymer formed increases with temperature and pH of the complex used. The effect of temperature, pH of the complex, amount of CCl_4 and amount of PVA used on the rate of polymerization investigated. The rate increases with increase in temperature and pH. The rate initially increased with increase in amount of CCl_4 and PVA and beyond a certain value it decreased. These values at which it occurred are 50 cc CCl_4 and 10 gm of PVA respectively. Thus it may be concluded that 50 cc CCl_4, PVA complex prepared by using 10 g PVA in 300 cc water, high temperature (around $80^{O}C$) and high pH (around 10) represent the optimum values for obtaining high graft yields and high rate of polymerization.

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APPENDIX
(TABLES AND FIGURES)

TABLE 1

Summary of Experimental Data

The experimental results have been presented in two parts:

In all three runs of part I, the samples were analysed to yield the weights of ungrafted PVA, graft copolymer and homopolymer (PMMA) and in runs 2 and 3, the molecular weights of the polymers have been determined.

Part II includes the results of the runs carried out to find the effect of 1) Reaction Temperature 2) Initial pH of the complex. 3) PVA concentration and 4) Amount of CCl_4 on the polymerization process.

Unless otherwise mentioned, the PVA-copper (II) complex used in the runs was prepared by using the following:

1) Poly (vinyl alcohol) - 10 gm in 300 cc water

2) $CuCl_2.2H_2O$ - 0.1657g in 100 cc water

3) NaOH solution - added as per the pH requirement of the complex.

20 ml of samples were withdrawn every half an hour. The first sample (at time t=0) was withdrawn after allowing the reactants to mix completely.

PART I

Run 1

i)   Temperature = $70^{o}C$

ii) pH of the complex = 9.26

iii) Reactor contents:

PVA complex	250 ml
CCl_4	50 ml
MMA	100 ml
Reactant volume =	400 ml

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.15	0.3409	0
0.5	6.9	0.4339	27.28
1.0	6.86	0.3684	8.07
2.0	6.46	0.4351	27.63
3.0	6.52	0.3895	14.26
4.0	6.15	0.3721	9.15
4.5	6.42	0.3684	8.07
5.0	6.28	0.3859	24.2

Time, t (in hours)	weight of ungrafted PVA (gm)	Weight of PMMA (gm)	Weight of graft copolymer (gm)
0	0.3264	0.0163	0.0286
0.5	0.3116	0.0298	0.0317
1.0	0.2487	0.0505	0.0398
2.0	0.2396	0.0849	0.0547
3.0	0.2203	0.0307	0.0651
4.0	0.2231	0.0472	0.0971

Run 2

i)   Temperature = 80°C

ii) pH of the complex = 10.1

iii) Reactor contents:

PVA complex	250 cc
CCl$_4$	50 cc
MMA	100 cc
Reactant volume =	400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.32	0.4289	0
0.5	6.92	0.4898	14.2
1.0	6.59	0.7939	85.1
1.5	6.38	1.2481	191
2.0	6.16	2.0898	387.2
2.5	6.15	2.8451	563
3.0	6.05	–	–
3.5	5.81	4.3518	914.6

Time, t (in hours)	weight of PVA (gm)	Weight of PMMA (gm)	Weight of graft copolymer (gm)
0	0.303	0.0826	0.0205
1.0	0.2519	0.2537	0.209
1.5	0.2493	0.2249	0.6556
2.0	0.2413	0.6976	0.6818
2.5	0.1755	0.8285	1.7763
3.5	0.1596	1.263	2.0926

Time, t (in hours)	Mol. wt. of PMMA Homopolymer $(\overline{M}_v)$	Mol. wt. of PMMA grafts $(\overline{M}_v)$
0	0.3705×10^5	3.92×10^5
1.0	5.37×10^5	9.55×10^5
1.5	10.25×10^5	10.6×10^5
2.0	13.44×10^5	11.6×10^5
2.5	14.05×10^5	14.35×10^5
3.5	13.71×10^5	18.2×10^5

Run 3

System: PVA - Styrene

i)   Temperature = $80^{\circ}C$

ii) pH of the complex = 10.18

iii) Reactor contents:

PVA complex	250 cc
CCl_4	50 cc
styrene	100 cc

Reactant volume =   400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)
0	8.37	1.0095
1.0	7.46	1.3709
2.25	7.01	1.3943
3.0	6.9	1.6807
4.0	6.48	1.5427
5.0	6.53	1.6129
6.0	6.34	0.9719
7.0	6.29	1.769
8.0	6.14	1.8877

Time, t (in hours)	weight of ungrafted PVA (gm)	Weight of Homopolymer (gm)	Weight of graft copolymer (gm)
0	0.5191	0.1368	0.3677
1.0	0.4501	0.1086	0.657
2.25	0.4378	0.1293	0.7336
3.0	0.3583	0.1237	0.8689
4.0	0.4536	0.1058	0.8942
5.0	0.4431	0.0555	0.5359
6.0	0.4264	0.0527	0.8377

Time, t (in hours)	Mol. wt. of polystyrene ($\overline{M}_v$)	Mol. wt. of polystyrene grafts ($\overline{M}_v$)
0	1.78×10^4	6.57×10^4
1.0	2.1×10^4	6.6×10^4
2.25	3.31×10^4	4.56×10^4
3.0	3.5×10^4	6.93×10^4
4.0	5.28×10^4	8.76×10^4
5.0	5.91×10^4	8.62×10^4
6.0	5.47×10^4	8.67×10^4

PART II

1) Effect of Temperature

System: PVA - Methyl methacrylate

Run **4**

i)   Temperature = 60°C

ii)   pH of the complex = **10.14**

iii) Reactor contents:

PVA complex	250 cc
CCl$_4$	50 cc
MMA	100 cc
Reactant volume =	400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.62	0.2408	0
0.5	7.32	0.3633	50.87
1.0	7.24	0.3155	31.02
1.5	7.11	0.3243	34.68
2.0	7.09	0.3259	35.34
2.5	7.09	0.3106	28.99
3.0	7.29	0.3108	29.07
3.5	7.02	0.3235	34.34
4.0	6.95	0.4415	83.35
5.0	6.98	0.4735	96.64

Run 5

i)   Temperature = $70^{\circ}C$

ii) pH of the complex = 10.17

iii) Reactor contents:

PVA complex	250 cc
CCl_4	50 cc
MMA	100 cc
Reactant volume =	400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.35	0.3278	0
0.5	6.8	0.3091	-
1.0	6.69	0.382	7.38
1.5	6.46	-	-
2.0	6.4	0.6027	83.86
2.5	6.36	0.9098	177.5
3.0	6.21	0.413	26.00
3.5	6.34	1.1235	242.7
4.0	6.2	1.3091	299.36
5.0	6.16	0.4043	23.34

Run 2

i)   Temperature = 80°C

ii) pH of the complex = 10.1

iii) Reactor contents:

PVA complex	250 cc
CCl_4	50 cc
MMA	100 cc
Reactant volume =	400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.32	0.4289	0
0.5	6.92	0.4898	14.2
1.0	6.59	0.7939	85.1
1.5	6.38	1.2481	191
2.0	6.16	2.0898	387.2
2.5	6.15	2.8451	563
3.0	6.05	–	–
3.5	6.81	4.3518	914.6

(After 3 hours, reaction mass become very viscous this caused difficulty in withdrawing samples and hence reaction was stopped after $3\frac{1}{2}$ hours).

2) EFFECT OF pH of the complex

   System: PVA-methyl methacrylate

Run 6

i)   Temperature = $70^{\circ}C$

ii) pH of the complex = 9.26

iii) Reactor contents:

PVA complex	250 cc
CCl_4	50 cc
MMA	100 cc
Reactant volume =	400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.15	0.3409	0
0.5	6.9	0.4339	27.28
1.0	6.86	0.3684	8.07
2.0	6.46	0.4351	27.63
3.0	6.52	0.3895	14.26
4.0	6.15	0.3721	9.15
4.5	6.42	0.3684	8.07
5.0	6.28	0.3859	24.2

Run 7

i) Temperature = $70^{o}C$

ii) pH of the complex = 8.02

iii) Reactor contents:

PVA complex	250 cc
CCl_4	50 cc
MMA	100 cc
Reactant volume =	400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.9	0.3153	0
0.5	7.54	0.3516	11.51
1.0	7.34	0.3221	2.16
1.5	7.26	0.318	0.86
2.0	7.15	0.323	2.442
2.5	7.10	0.3241	2.79
3.5	6.94	0.3363	6.667
4.0	6.91	0.3618	.14.75

Run 5

i)   Temperature = $70^{\circ}C$

ii) pH of the complex = 10.17

iii) Reactor contents:

PVA complex	250 cc
CCl_4	50 cc
MMA	100 cc

Reactant volume = 400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.35	0.3278	0
0.5	6.8	0.3091	--
1.0	6.69	0.382	7.38
1.5	6.46	–	--
2.0	6.4	0.6027	83.86
2.5	6.36	0.9098	177.5
3.0	6.21	0.413	26.00
3.5	6.34	1.1235	242.7
4.0	6.2	1.3091	299.36
5.0	6.16	0.4043	23.34

3) EFFECT OF AMOUNT OF PVA (PVA CONCENTRATION)

System: PVA methyl methacrylate

Run 8

i)   Temperature = $70^{\circ}C$

ii) pH of the complex = 10.24

iii) Reactor contents:

     PVA complex (prepared from   250 cc

     i) 5 gm PVA in 300 cc water

     ii) 0.0829 g $CuCl_2 . 2H_2O$ in 100 cc water

     iii) NaOH solution to adjust pH)

     CCl_4 50 cc

     MMA   100 cc

     Reactant volume =   400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.99	0.1728	0
0.5	7.61	0.2097	21.35
1.0	7.5	0.197	14.00
1.5	7.2	0.2859	65.45
2.0	7.16	0.2736	58.33
2.5	7.1	0.2737	58.39
3.0	7.17	0.2549	47.51
3.5	6.95	0.2983	72.63
4.0	7.00	0.2616	51.39

Run 9

i)   Temperature = $70^{\circ}C$

ii) pH of the complex = 10.17

iii) Reactor contents:

PVA complex (prepared from	250 cc

    i) 15 gm PVA in 300 cc water

     ii) 0.2486 g $CuCl_2$. $2H_2O$ in 100 cc water

      iii) NaOH solution to adjust pH)

CCl_4	50 cc
MMA	100 cc

Reactant volume = 400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	8.12	0.2437	0
0.5	7.18	0.502	106
1.0	7.07	0.3814	56.5
1.5	6.95	0.3772	54.78
2.0	6.86	0.539	121.2
2.5	6.78	0.5318	118.2
3.0	6.72	0.3441	41.2
3.5	6.68	0.5429	122.8
4.0	6.70	0.2969	21.83

Run 5

i)   Temperature = 70°C

ii) pH of the complex = 10.17

iii) Reactor contents:

      PVA complex (prepared from   250 cc

       i) 10 g PVA in 300 cc water

        ii) 0.1657 g of $CuCl_2 . 2H_2O$ in 100 cc water

         iii) NaOH solution to adjust pH of the complex)

           CCl_4 50 cc

           MMA   100 cc

           Reactant volume =   400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.35	0.3278	0
0.5	6.8	0.3091	–
1.0	6.69	0.382	7.38
1.5	6.46	–	–
2.0	6.4	0.6027	83.86
2.5	6.36	0.9098	177.5
3.0	6.21	0.413	26.00
3.5	6.34	1.1235	242.7
4.0	6.2	1.3091	299.36
5.0	6.16	0.4043	23.34

4) EFFECT OF AMOUNT OF CCL_4

System: PVA methyl methacrylate

Run 10

i)   Temperature = $70^{\circ}C$

ii) pH of the complex = 10.09

iii) Reactor contents:

PVA complex	250 cc
CCl_4	65 cc
MMA	100 cc
Reactant volume =	415 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.31	0.2217	0
0.5	6.94	0.3724	67.97
1.0	6.91	0.3004	35.5
1.5	6.7	0.3176	43.26
2.0	6.78	0.2905	31.03
2.5	6.66	0.4257	92.02
3.0	6.55	0.3113	40.41
3.5	6.52	0.4417	99.23
4.0	6.51	0.4495	102.75
5.0	6.55	0.4824	117.6

Run 11

i)   Temperature = $70^{o}C$

ii) pH of the complex = 10.17

iii) Reactor contents:

PVA complex	250 cc
CCl_4	25 cc
MMA	100 cc
Reactant volume =	375 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.6	0.3267	0
0.5	7.21	0.3468	6.15
1.0	7.17	0.4061	24.3
1.5	6.94	0.3641	11.45
2.0	6.83	0.3838	17.48
2.5	6.77	0.371	13.56
3.0	6.71	0.4394	34.5
3.5	6.58	0.392	19.99
4.0	6.75	0.6326	33.63
5.0	6.64	0.463	41.72

Run 12

i)   Temperature = 70°C

ii) pH of the complex = 10.24

iii) Reactor contents:

PVA complex	250 cc
CCl_4	0 cc
MMA	100 cc
Reactant volume =	350 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.72	0.3013	0
0.5	7.36	0.3561	18.19
1.0	7.41	0.3144	4.35
1.5	7.34	0.3943	30.87
2.0	7.21	0.365	21.14
3.5	0.83	0.4231	40.43
4.0	6.81	0.381	26.45

Run 5

i)   Temperature = $70^{\circ}C$

ii) pH of the complex = 10.17

iii) Reactor contents:

PVA complex	250 cc
CCl_4	50 cc
MMA	100 cc
Reactant volume =	400 cc

Time, t (in hours)	pH of the sample	Weight of dried sample (gm)	% increase in weight
0	7.35	0.3278	0
0.5	6.8	0.3091	–
1.0	6.69	0.382	7.38
1.5	6.46	–	–
2.0	6.4	0.6027	83.86
2.5	6.36	0.9098	177.5
3.0	6.21	0.413	26.00
3.5	6.34	1.1235	242.7
4.0	6.2	1.3091	299.36
5.0	6.16	0.4043	23.34

TABLE 2

KINETIC MODEL FOR GRAFTING OF PVA

a) Diffusion of CCl_4 from droplet to water phase

$$CCl_4^d \rightleftarrows CCl_4^W \quad \text{mass transfer coefficient : KK1}$$
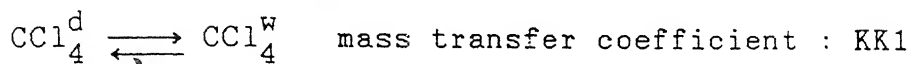
b) Initiation with CCl_4

$$CCl_4^W + OH_c^W \xrightarrow{K_3} R_G^W\cdot + \cdot CCl_3^W$$
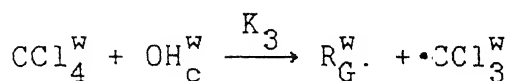
c) Diffusion of monomer from droplet to water phase

$$M^d \rightleftarrows M^W \quad \text{mass transfer coefficient : KK2}$$
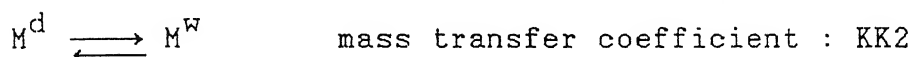
d) Generation of polymer radicals

$$\cdot CCl_3^d + M^d \xrightarrow{K_5} P_1^d$$

$$\cdot CCl_3^W + M^W \xrightarrow{k_6} P_1^W\cdot$$

$$R_G^W\cdot + M^W \xrightarrow{K_7} R_G P_1^W$$
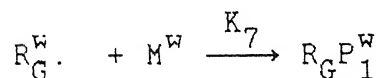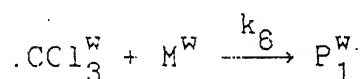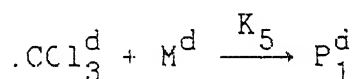
Propagation

Aqueous phase

$$R_G P_1^W + M^W \xrightarrow{K_{11}} R_G P_2^W + M^W \longrightarrow\rightarrow\rightarrow R_G P_n^W$$

$$P_1^W + M^W \xrightarrow{K_{12}} P_2^W + M^W \longrightarrow\rightarrow\rightarrow P_n^W$$

Droplet phase

$$R_G P_1^d + M^d \xrightarrow{K_{13}} R_G P_2^d + M^d \longrightarrow\rightarrow\rightarrow R_G P_n^d$$

$$P_1^d + M^d \xrightarrow{K_{14}} P_2^d + M^d \longrightarrow\rightarrow\rightarrow P_n^d$$
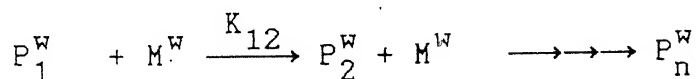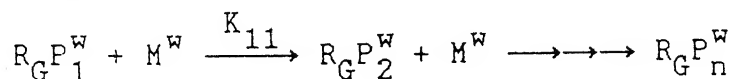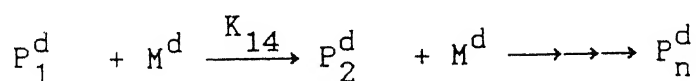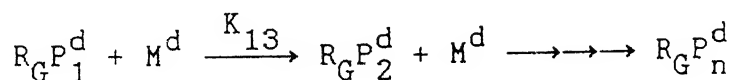
Radical diffusion between phases

$$R_GP_n^W \rightleftarrows R_GP_n^d \qquad \text{Mass transfer coefficient : KK9}$$

$$P_n^W \rightleftarrows P_n^d \qquad \text{Mass transfer coefficient : KK10}$$
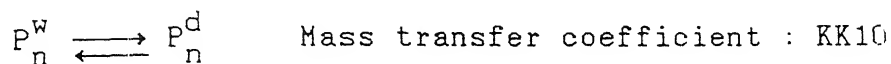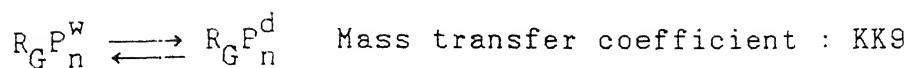
Termination

a) By disproportionation

Aqueous phase

$$R_GP_n^W + R_GP_m^W \xrightarrow{K_{15}} R_GM_n^W + R_GM_m^W$$

$$R_GP_n^W + P_m^W \xrightarrow{K_{16}} R_GM_n^W + M_m^W$$

$$P_m^W + P_n^W \xrightarrow{K_{17}} M_n^W + M_m^W$$

Droplet phase

$$R_GP_n^d + R_GP_m^d \xrightarrow{K_{18}} R_GM_n^d + R_GM_m^d$$

$$R_GP_n^d + P_m^d \xrightarrow{K_{19}} R_GM_n^d + M_m^d$$

$$P_m^d + P_n^d \xrightarrow{K_{20}} M_m^d + M_n^d$$
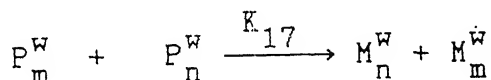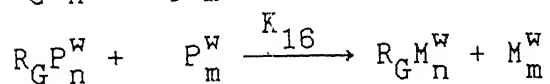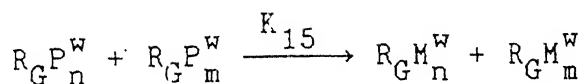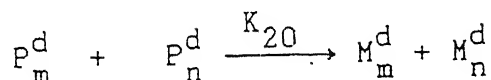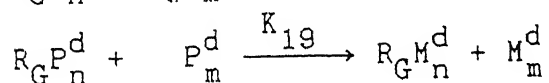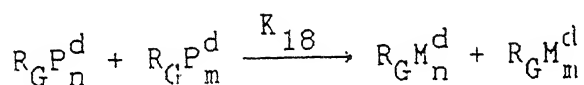
b) By combination

Aqueous phase

$$R_GP_n^W + P_m^W \xrightarrow{K_{22}} R_GM_{m+n}^W$$

$$P_n^W + P_m^W \xrightarrow{K_{23}} M_{m+n}^W$$

Droplet phase

$$R_GP_n^d + P_m^d \xrightarrow{K_{25}} R_GM_{m+n}^d$$

$$P_n^d + P_m^d \xrightarrow{K_{26}} M_{m+n}^d$$
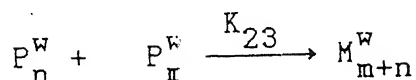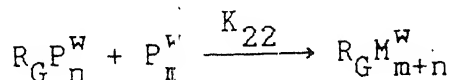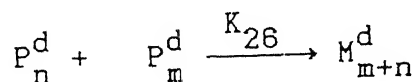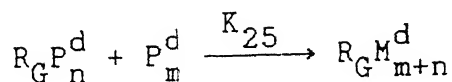
Chain Transfer Reactions

a)   With CCl_4

Droplet phase

$$R_G P_n^d + CCl_4^d \xrightarrow{K_{27}} R_G M_n^d + .CCl_3^d$$

$$P_n^d + CCl_4^d \xrightarrow{K_{28}} M_n^d + .CCl_3^d$$

Aqueous phase

$$R_G P_n^w + CCl_4^w \xrightarrow{K_{35}} R_G M_n^w + .CCl_3^w$$

$$P_n^w + CCl_4^w \xrightarrow{K_{36}} M_n^w + .CCl_3^w$$
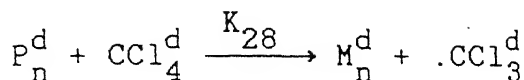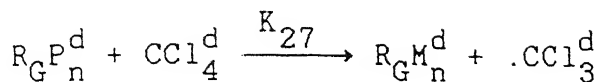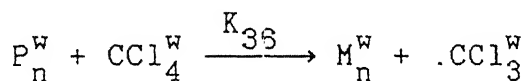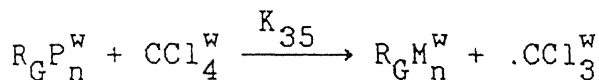
b)   With monomer

Droplet phase

$$R_G P_n^d + M^d \xrightarrow{K_{29}} R_G M_n^d + P_1^d$$

$$P_n^d + M^d \xrightarrow{K_{30}} M_n^d + P_1^d$$

Aqueous phase

$$R_G P_n^w + M^w \xrightarrow{K_{41}} R_G M_n^w + P_1^w$$

$$P_n^w + M^w \xrightarrow{K_{42}} M_n^w + P_1^w$$
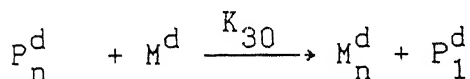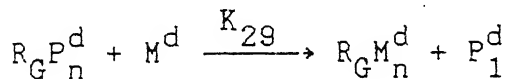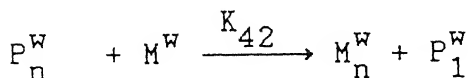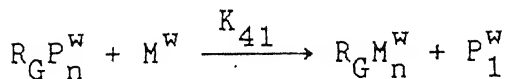
c)   With dead polymer

Droplet phase

$$R_G P_n^d + M_m^d \xrightarrow{K_{31}} R_G M_n^d + P_m^d$$

$$P_n^d + M_m^d \xrightarrow{K_{33}} M_n^d + P_m^d$$

$$P_n^d + R_G M_m^d \xrightarrow{K_{34}} M_n^d + R_G P_m^d$$

Aqueous phase

$$R_G P_n^W + R_G M_m^W \xrightarrow{K_{38}} R_G M_n^W + R_G P_m^W$$

$$P_n^W + M_m^W \xrightarrow{K_{39}} M_n^W + P_m^W$$

$$R_G M_m^W + P_n^W \xrightarrow{K_{40}} R_G P_m^W + M_n^W$$
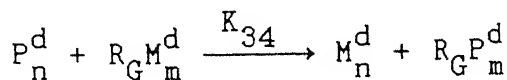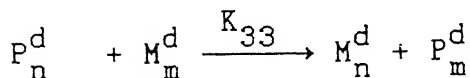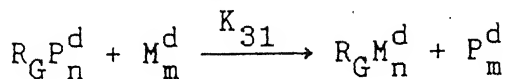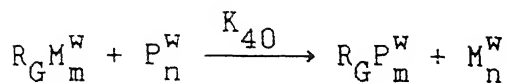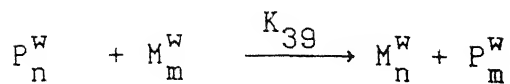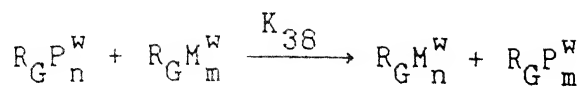
Diffusion of dead polymer species from droplet to water phase

$$M_n^d \rightleftharpoons M_n^W \qquad \text{Mass transfer coefficient : KK49}$$

$$R_G M_n^d \rightleftharpoons R_G M_n^W \qquad \text{Mass transfer coefficient : KK50}$$
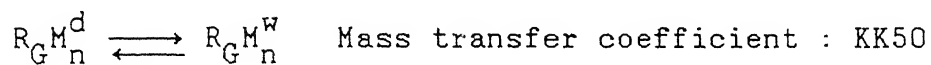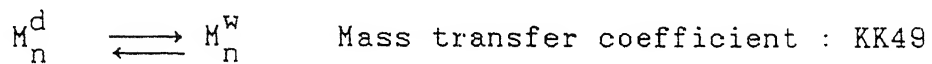
TABLE 3

MOLE BALANCE EQUATIONS FOR THE MOLECULAR SPECIES

1) Balance for CCl_4

a) Aqueous phase

$$\frac{d}{dt}[CCl_4^W] = V\{-K_3[CCl_4^W][OH_c^W]-K_{35}[CCl_4^W]\lambda_{R_GP_{no}^W}-K_{36}[CCl_4^W]\lambda_{P_{no}^W}\}$$

$$+ KK1\{[CCl_4^d]-[CCl_4^W]\} \tag{1}$$

b) Droplet phase

$$\frac{d}{dt}[CCl_4^d] = (1-V)\{-K_{27}[CCl_4^d]\lambda_{R_GP_{no}^d}-K_{28}[CCl_4^d]\lambda_{P_{no}^d}\}$$

$$-KK1\{[CCl_4^d] - [CCl_4^W]\} \tag{2}$$

2) Balance for monomer

a) Aqueous phase

$$\frac{d}{dt}[M^W] = V\{-K_6[.CCl_3^W][M^W]-K_7[R_G^W.][M^W]-K_{11}[M^W]\lambda_{R_GP_{no}^W}$$

$$-K_{12}[M^W]\lambda_{P_{no}^W}-K_{41}[M^W]\lambda_{R_GP_{no}^W}-K_{42}[M^W]\lambda_{P_{no}^W}\}$$

$$+KK2\{[M^d]-[M^W]\} \tag{3}$$

b) Droplet phase

$$\frac{d}{dt}[M^d] = (1-V)\{-K_5[.CCl_3^d][M^d]-K_{13}[M^d]\lambda_{R_GP_{no}^d}-K_{14}[M^d]\lambda_{P_{no}^d}$$

$$-K_{29}[M^d]\lambda_{R_GP_{no}^d}-K_{30}[M^d]\lambda_{P_{no}^d}\}-KK2\{[M^d]-[M^W]\} \tag{4}$$

3) Balance for PVA (aqueous phase)

$$\frac{d}{dt}[OH_c^W]= - VK_3[CCl_4^W][OH_c^W] \tag{5}$$

4) Balance for dead homopolymer

a) Aqueous phase

$$\frac{d}{dt}[M_n^W] = V\{K_{16}[P_n^W][\sum_{r=1}^{\infty} R_G P_r^W] + K_{17}[P_n^W][\sum_{r=1}^{\infty} P_r^W] + K_{23}\sum_{r=1}^{\infty}[P_r^W][P_{n-r}^W]$$

$$+ K_{36}[P_n^W][CCl_4^W] + K_{42}[P_n^W][M^W] - K_{37}[M_n^W][\sum_{r=1}^{\infty} R_G P_r^W]$$

$$+ K_{40}[P_n^W][\sum_{r=1}^{\infty} R_G M_r^W] + K_{39}[P_n^W][\sum_{r=1}^{\infty} M_r^W] - K_{39}[M_n^W][\sum_{r=1}^{\infty} P_r^W]\}$$

$$+ KK49\{[M_n^d] - [M_n^W]\} \tag{A}$$

b) Droplet phase

$$\frac{d}{dt}[M_n^d] = (1-V)\{K_{19}[P_n^d][\sum_{r=1}^{\infty} R_G P_r^d] + K_{28}[P_n^d][CCl_4^d] + K_{30}[P_n^d][M^d]$$

$$+ K_{20}[P_n^d][\sum_{r=1}^{\infty} M_r^d] + K_{26}\sum_{r=1}^{n-1}[P_r^d][P_{n-r}^d] - K_{31}[M_n^d][\sum_{r=1}^{\infty} R_G P_r^d]$$

$$+ K_{34}[P_n^d][\sum_{r=1}^{\infty} R_G M_r^d] + K_{33}[P_n^d][\sum_{r=1}^{\infty} M_r^d]$$

$$- K_{33}[M_n^d][\sum_{r=1}^{\infty} P_r^d]\} - KK49\{[M_n^d] - [M_n^W] \tag{B}$$

5) Balance for dead graft copolymer

a) Aqueous phase

$$\frac{d}{dt}[R_G M_n^W] = V\{K_{15}[R_G P_n^W][\sum_{r=1}^{\infty} R_G P_r^W] + K_{16}[R_G P_n^W][\sum_{r=1}^{\infty} P_r^W]$$

$$+ K_{22}\sum_{r=1}^{n-1}[R_G P_r^W][P_{n-r}^W] + K_{35}[R_G P_n^W][CCl_4^W]$$

$$+ K_{41}[R_G P_n^W][M^W] + K_{37}[R_G P_n^W][\sum_{r=1}^{\infty} M_r^W] - K_{40}[R_G M_n^W][\sum_{r=1}^{\infty} P_r^W]$$

$$+ K_{38}[R_G P_n^W][\sum_{r=1}^{\infty} R_G M_r^W] - K_{38}[R_G M_n^W][\sum_{r=1}^{\infty} R_G P_r^W]\}$$

$$+ KK50\{[R_G M_n^d] - [R_G M_n^W]\} \tag{C}$$

b)   Droplet phase

$$\frac{d}{dt}[R_G M_n^d] = (1-V)\{K_{19}[R_G P_n^d][\sum_{r=1}^{\infty} P_r^d] + K_{25} \sum_{r=1}^{n-1} [R_G P_r^d][P_{n-r}^d]$$

$$+K_{18}[R_G P_n^d][\sum_{r=1}^{\infty} R_G P_r^d] + K_{27}[R_G P_n^d][CC1_4^d]$$

$$+K_{29}[\sum_{n=1}^{\infty} R_G P_n^d][M^d] + K_{31}[R_G P_n^d][\sum_{r=1}^{\infty} M_r^d]$$

$$-K_{34}[R_G M_n^d][\sum_{r=1}^{\infty} P_r^d]\} - KK50\{[R_G M_n^d] - [R_G M_n^w]\} \qquad (D)$$

TABLE 4

MOMENT EQUATIONS FOR THE DEAD POLYMER SPECIES (DERIVED FROM EQS. (A), (B), (C) AND (D))

1) Dead Homopolymer

a) Aqueous phase

ZEROTH MOMENT

$$\frac{d}{dt}(\lambda_{M_{no}^w}) = V\{K_{16}\lambda_{R_G P_{no}^w}\lambda_{P_{no}^w} + (K_{17}+K_{23})\lambda_{P_{no}^w}^2 + K_{36}[CCl_4^w]\lambda_{P_{no}^w}$$

$$+K_{42}[M^w]\lambda_{P_{no}^w} - K_{37}\lambda_{M_{no}^w}\lambda_{R_G P_{no}^w} + K_{40}\lambda_{R_G M_{no}^w}\lambda_{P_{no}^w}\}$$

$$+KK49(\lambda_{M_{no}^d} - \lambda_{M_{no}^w}) \tag{6}$$

FIRST MOMENT

$$\frac{d}{dt}(\lambda_{M_{n1}^w}) = V\{K_{16}\lambda_{R_G P_{no}^w}\lambda_{P_{n1}^w} + K_{17}\lambda_{P_{no}^w}\lambda_{P_{n1}^w} + 2K_{23}\lambda_{P_{no}^w}\lambda_{P_{n1}^w}$$

$$+K_{36}[CCl_4^w]\lambda_{P_{n1}^w} + K_{42}[M^w]\lambda_{P_{n1}^w} - K_{37}\lambda_{M_{n1}^w}\lambda_{R_G P_{no}^w}$$

$$+K_{40}\lambda_{R_G M_{no}^w}\lambda_{P_{n1}^w} + K_{39}\lambda_{M_{no}^w}\lambda_{P_{n1}^w} - K_{39}\lambda_{P_{no}^w}\lambda_{M_{n1}^w}\}$$

$$+KK49(\lambda_{M_{n1}^d} - \lambda_{M_{n1}^w}) \tag{7}$$

SECOND MOMENT

$$\frac{d}{dt}(\lambda_{M_{n2}^w}) = V\{K_{16}\lambda_{R_G P_{no}^w}\lambda_{P_{n2}^w} + K_{17}\lambda_{P_{no}^w}\lambda_{P_{n2}^w} + 2K_{23}\lambda_{P_{no}^w}\lambda_{P_{n2}^w}$$

$$+2K_{23}\lambda_{P_{n1}^w}^2 + K_{36}[CCl_4^w]\lambda_{P_{n2}^w} + K_{42}[M^w]\lambda_{P_{n2}^w} - K_{37}\lambda_{M_{n2}^w}\lambda_{R_G P_{no}^w}$$

$$+K_{40}\lambda_{R_G M_{no}^w}\lambda_{P_{n2}^w} + K_{39}\lambda_{M_{no}^w}\lambda_{P_{n2}^w} - K_{39}\lambda_{P_{no}^w}\lambda_{M_{n2}^w}\}$$

$$+KK49(\lambda_{M_{n2}^d} - \lambda_{M_{n2}^w}) \tag{8}$$

b)   Droplet phase

ZEROTH MOMENT

$$\frac{d}{dt}(\lambda_{M^d_{no}}) = (1-V)\{K_{19}\lambda_{P^d_{no}}\lambda_{R_G P^d_{no}} + K_{28}[CCl^d_4]\lambda_{P^d_{no}} + (K_{20}+K_{26})\lambda^2_{P^d_{no}}$$

$$+ K_{30}[M^d]\lambda_{P^d_{no}} - K_{31}\lambda_{R_G P^d_{no}}\lambda_{M^d_{no}} + K_{34}\lambda_{R_G M^d_{no}}\lambda_{P^d_{no}}\}$$

$$- KK49(\lambda_{M^d_{no}} - \lambda_{M^w_{no}}) \tag{9}$$

FIRST MOMENT

$$\frac{d}{dt}(\lambda_{M^d_{n1}}) = (1-V)\{K_{19}\lambda_{P^d_{n1}}\lambda_{R_G P^d_{no}} + K_{28}[CCl^d_4]\lambda_{P^d_{n1}} + K_{20}\lambda_{P^d_{no}}\lambda_{P^d_{n1}}$$

$$+ 2K_{26}\lambda_{P^d_{no}}\lambda_{P^d_{n1}} + K_{30}[M^d]\lambda_{P^d_{n1}} - K_{31}\lambda_{R_G P^d_{no}}\lambda_{M^d_{n1}}$$

$$+ K_{34}\lambda_{R_G M^d_{no}}\lambda_{P^d_{n1}} + K_{33}\lambda_{M^d_{no}}\lambda_{P^d_{n1}} - K_{33}\lambda_{P^d_{no}}\lambda_{M^d_{n1}}$$

$$- KK49(\lambda_{M^d_{n1}} - \lambda_{M^w_{n1}}) \tag{10}$$

SECOND MOMENT

$$\frac{d}{dt}(\lambda_{M^d_{n2}}) = (1-V)\{K_{19}\lambda_{P^d_{n2}}\lambda_{R_G P^d_{no}} + K_{28}[CCl^d_4]\lambda_{P^d_{n2}} + K_{30}[M^d]\lambda_{P^d_{n2}}$$

$$- K_{31}\lambda_{R_G P^d_{no}}\lambda_{M^d_{n2}} + K_{34}\lambda_{R_G M^d_{no}}\lambda_{P^d_{n2}} + K_{33}\lambda_{M^d_{no}}\lambda_{P^d_{n2}}$$

$$- K_{33}\lambda_{P^d_{no}}\lambda_{M^d_{n2}}\} - KK49(\lambda_{M^d_{n2}} - \lambda_{M^w_{n2}}) \tag{11}$$

2)   Dead Graft Copolymer

a)   Aqueous phase

ZEROTH MOMENT

$$\frac{d}{dt}(\lambda_{R_G M^w_{no}}) = V\{K_{15}\lambda^2_{R_G P^w_{no}} + K_{16}\lambda_{P^w_{no}}\lambda_{R_G P^w_{no}} + K_{22}\lambda_{R_G P^w_{no}}\lambda_{P^w_{no}}$$

$$+ K_{35}[CCl^w_4]\lambda_{R_G P^w_{no}} + K_{41}[M^w]\lambda_{R_G P^w_{no}} + K_{37}\lambda_{M^w_{no}}\lambda_{R_G P^w_{no}}$$

$$- K_{40}\lambda_{P^w_{no}}\lambda_{R_G P^w_{no}}\} + KK50(\lambda_{R_G M^d_{no}} - \lambda_{R_G M^w_{no}}) \tag{12}$$

FIRST MOMENT

$$\frac{d}{dt}((\lambda_{R_G M^d_{n1}}) = (1-V)(K_{19}\lambda_{R_G P^d_{n1}}\lambda_{P^d_{no}} + K_{25}\lambda_{R_G P^d_{no}}\lambda_{P^d_{n1}}$$

$$+K_{25}\lambda_{R_G P^d_{n1}}\lambda_{P^d_{no}} + K_{27}[CCl^d_4]\lambda_{R_G P^d_{n1}} + K_{29}[M^d]\lambda_{R_G P^d_{no}}$$

$$+K_{31}\lambda_{M^d_{no}}\lambda_{R_G P^d_{no}}) + K_{18}\lambda_{R_G P^d_{no}}\lambda_{R_G P^d_{n1}} - K_{34}\lambda_{P^d_{no}}\lambda_{R_G M^d_{n1}}\}$$

$$-KK50(\lambda_{R_G M^d_{n1}} - \lambda_{R_G M^w_{n1}}) \tag{16}$$

SECOND MOMENT

$$\frac{d}{dt}((\lambda_{R_G M^d_{n2}}) = (1-V)(K_{19}\lambda_{R_G P^d_{n2}}\lambda_{P^d_{no}} + K_{25}\lambda_{R_G P^d_{no}}\lambda_{P^d_{n2}}$$

$$+2K_{25}\lambda_{R_G P^d_{n1}}\lambda_{P^d_{n1}} + K_{25}\lambda_{P^d_{no}}\lambda_{R_G P^d_{n2}} + K_{27}[CCl^d_4]\lambda_{R_G P^d_{n2}}$$

$$+K_{29}[M^d]\lambda_{R_G P^d_{no}} + K_{31}\lambda_{M^d_{no}}\lambda_{R_G P^d_{n2}} - K_{34}\lambda_{P^d_{no}}\lambda_{R_G M^d_{n2}}$$

$$-KK50(\lambda_{R_G M^d_{n2}} - \lambda_{R_G M^w_{n2}}) \tag{17}$$

TABLE 5

BALANCE FOR THE INTERMEDIATE SPECIES

Since according to the steady state approximation rate of change of the intermediate species is zero, we get fifteen algebraic equations which are as follows:

ALGEBRAIC EQUATIONS

1) Balance for $R_G^W \cdot$

$$V\{-K_7[R_G^W \cdot][M^W] + K_3[CCl_4^W][OH_c^W]\} = 0$$

i.e., $[R_G^W] = \dfrac{K_3[CCl_4^W][OH_c^W]}{K_7[M^W]}$ \hfill (I)

2) Balance for $.CCl_3^d$

$$(1-V)\{K_{27}[CCl_4^d]\lambda_{R_G P_{no}^d} + K_{28}[CCl_4^W]\lambda_{P_{no}^d} - K_5[.CCl_3^d][M^d]\} = 0$$

i.e., $[.CCl_3^d] = \dfrac{\{K_{27}[CCl_4^d]\lambda_{R_G P_{no}^d} + K_{28}[CCl_4^d]\lambda_{P_{no}^d}\}}{K_5[M^d]}$ \hfill (II)

3) Balance for $.CCl_3^W$

$$V\{-K_6[.CCl_3^W][M^d] + K_3[CCl_4^W][OH_c^W] + K_{35}[CCl_4^W]\lambda_{R_G P_{no}^d}$$

$$+K_{36}[CCl_4^W]\lambda_{P_{no}^W}\} = 0$$

i.e. $[.CCl_3^W] = \dfrac{K_3[CCl_4^W][OH_c^W] + K_{35}[CCl_4^W]\lambda_{R_G P_{no}^W} + K_{36}[CCl_4^W]\lambda_{P_{no}^W}}{K_6[M^d]}$ \hfill (III)

4) Moment equations for P_n^d

ZEROTH MOMENT

$$(1-V)\{K_{13}[CC1_3^d][M^d]-(K_{19}+K_{25})\lambda_{R_GP_{no}^d}\lambda_{P_{no}^d}-K_{28}[CC1_4^d]\lambda_{P_{no}^d}$$

$$-(K_{20}+K_{26})\lambda_{P_{no}^d}^2+K_{31}\lambda_{R_GP_{no}^d}\lambda_{M_{no}^d}-K_{34}\lambda_{P_{no}^d}\lambda_{R_GM_{no}^d}$$

$$+K_{29}[M^d]\lambda_{R_GP_{no}^d}\}-KK10(\lambda_{P_{no}^d}-\lambda_{P_{no}^w})=0 \qquad (IV)$$

FIRST MOMENT

$$(1-V)\{K_{13}[CC1_3^d][M^d]+(K_{14}[M^d]\lambda_{P_{no}^d}-(K_{19}+K_{25})\lambda_{R_GP_{no}^d}\lambda_{P_{n1}^d}$$

$$-(K_{20}+K_{26})\lambda_{P_{no}^d}\lambda_{P_{n1}^d}-K_{28}[CC1_4^d]\lambda_{P_{n1}^d}+K_{31}\lambda_{R_GP_{no}^d}\lambda_{M_{n1}^d}$$

$$-K_{34}\lambda_{P_{n1}^d}\lambda_{R_GM_{no}^d}-K_{33}\lambda_{M_{no}^d}\lambda_{P_{n1}^d}+K_{33}\lambda_{P_{no}^d}\lambda_{M_{n1}^d}$$

$$+K_{29}[M^d]\lambda_{R_GP_{no}^d}\}-KK10(\lambda_{P_{n1}^d}-\lambda_{P_{n1}^w})=0 \qquad (V)$$

SECOND MOMENT

$$(1-V)\{K_{13}[CC1_3^d][M^d]+2K_{14}[M^d]\lambda_{P_{n1}^d}+K_{14}[M^d]\lambda_{P_{no}^d}$$

$$-(K_{19}+K_{25})\lambda_{R_GP_{no}^d}\lambda_{P_{n2}^d}-(K_{20}+K_{26})\lambda_{P_{no}^d}\lambda_{P_{n2}^d}$$

$$-K_{28}[CC1_4^d]\lambda_{P_{n2}^d}+K_{31}\lambda_{R_GP_{no}^d}\lambda_{M_{n2}^d}-K_{34}\lambda_{R_GM_{no}^d}\lambda_{P_{n2}^d}$$

$$-K_{33}\lambda_{M_{no}^d}\lambda_{P_{n2}^d}+K_{33}\lambda_{P_{no}^d}\lambda_{M_{n2}^d}+K_{29}[M^d]\lambda_{R_GP_{no}^d}\}$$

$$-KK10(\lambda_{P_{n2}^d}-\lambda_{P_{n2}^w})=0 \qquad (VI)$$

5) Moment Equations for $R_GP_n^d$

ZEROTH MOMENT

$$(1-V)\{-(K_{19}+K_{25})\lambda_{P_{no}^d}\lambda_{R_GP_{no}^d}-K_{27}[CC1_4^d]\lambda_{R_GP_{no}^d}$$

$$-K_{29}[M^d]\lambda_{R_GP_{no}^d}-K_{18}\lambda_{R_GP_{no}^d}^2-K_{31}\lambda_{M_{no}^d}\lambda_{R_GP_{no}^d}$$

$$+K_{34}\lambda_{P_{no}^d}\lambda_{R_GM_{no}^d}\}-KK9(\lambda_{R_GP_{no}^d}-\lambda_{R_GP_{no}^w})=0 \qquad (VII)$$

FIRST MOMENT

$$(1-V)\{K_{13}[M^d]\lambda_{R_GP_{no}^d} - (K_{19}+K_{25})\lambda_{P_{no}^d}\lambda_{R_GP_{n1}^d} - K_{27}[CCl_4^d]\lambda_{R_GP_{n1}^d}$$

$$-K_{29}[M^d]\lambda_{R_GP_{n1}^d} - K_{18}\lambda_{R_GP_{no}^d}\lambda_{R_GP_{n1}^d} - K_{31}\lambda_{M_{no}^d}\lambda_{R_GP_{n1}^d}$$

$$+K_{34}\lambda_{P_{no}^d}\lambda_{R_GM_{n1}^d}\} - KK9(\lambda_{R_GP_{n1}^d} - \lambda_{R_GP_{n1}^w}) = 0 \qquad (VIII)$$

SECOND MOMENT

$$(1-V)\{2K_{13}[M^w]\lambda_{R_GP_{n1}^d} + K_{13}[M^w]\lambda_{R_GP_{no}^d} - (K_{19}+K_{25})\lambda_{P_{no}^d}\lambda_{R_GP_{n2}^d}$$

$$-K_{27}[CCl_4^d]\lambda_{R_GP_{n2}^d} - K_{18}\lambda_{R_GP_{no}^d}\lambda_{R_GP_{n2}^d} - K_{29}[M^d]\lambda_{R_GP_{n2}^d}$$

$$-K_{31}\lambda_{M_{no}^d}\lambda_{R_GP_{n2}^d} + K_{34}\lambda_{P_{no}^d}\lambda_{R_GM_{n2}^d}\} - KK9(\lambda_{R_GP_{n2}^d} - \lambda_{R_GP_{n2}^w}) = 0 \qquad (IX)$$

6) Moment Equations for P_n^w

ZEROTH MOMENT

$$V(K_6[.CCl_3^w][M^w] - (K_{16}+K_{22})\lambda_{R_GP_{no}^w}\lambda_{P_{no}^w} - (K_{17}+K_{23})\lambda_{P_{no}^w}^2$$

$$-K_{36}[CCl_4^w]\lambda_{P_{no}^w} + K_{37}\lambda_{R_GP_{no}^w}\lambda_{M_{no}^w} - K_{40}\lambda_{R_GM_{no}^w}\lambda_{P_{no}^w}$$

$$+K_{41}[M^d]\lambda_{R_GP_{no}^w}\} + KK10(\lambda_{P_{no}^d} - \lambda_{P_{no}^w}) = 0 \qquad (X)$$

FIRST MOMENT

$$V(K_6[.CCl_3^w][M^w] - (K_{16}+K_{22})\lambda_{R_GP_{no}^w}\lambda_{P_{n1}^w} + K_{12}[M^w]\lambda_{P_{no}^w}$$

$$-(K_{17}+K_{23})\lambda_{P_{no}^w}\lambda_{P_{n1}^w} - K_{36}[CCl_4^w]\lambda_{P_{n1}^w} + K_{37}\lambda_{R_GP_{no}^w}\lambda_{M_{n1}^w}$$

$$-K_{40}\lambda_{R_GM_{no}^w}\lambda_{P_{n1}^w} - K_{39}\lambda_{M_{no}^w}\lambda_{P_{n1}^w} + K_{39}\lambda_{P_{no}^w}\lambda_{M_{n1}^w}$$

$$+K_{41}[M^w]\lambda_{R_GP_{no}^w}\} + KK10(\lambda_{P_{n1}^d} - \lambda_{P_{n1}^w}) = 0 \qquad (XI)$$

SECOND MOMENT

$$V\{K_6[.CCl_3^w][M^w]+2K_{12}[M^w]\lambda_{P_{n1}^w}+K_{12}[M^w]\lambda_{P_{no}^w}$$

$$-(K_{16}+K_{22})\lambda_{R_GP_{no}^w}\lambda_{P_{n2}^w}-K_{36}[CCl_4^w]\lambda_{P_{n2}^w}+K_{37}\lambda_{R_GP_{no}^w}\lambda_{M_{n1}^w}$$

$$-(K_{17}+K_{23})\lambda_{P_{no}^w}\lambda_{P_{n2}^w}-K_{40}\lambda_{R_GM_{no}^w}\lambda_{P_{n2}^w}-K_{39}\lambda_{M_{no}^w}\lambda_{P_{n2}^w}$$

$$+K_{39}\lambda_{P_{no}^w}\lambda_{M_{n2}^w}+K_{41}[M^w]\lambda_{R_GP_{no}^w}\}+KK10(\lambda_{P_{n2}^d}-\lambda_{P_{n2}^w})=0 \qquad .(XII)$$

7) Moment Equations for $R_GP_n^w$

ZEROTH MOMENT

$$V\{K_7[R_G^w.][M^w]-K_{15}\lambda_{R_GP_{no}^w}^2-(K_{16}+K_{22})\lambda_{P_{no}^w}\lambda_{R_GP_{no}^w}$$

$$-K_{35}[CCl_4^w]\lambda_{R_GP_{no}^w}-K_{41}[M^w]\lambda_{R_GP_{no}^w}-K_{37}\lambda_{M_{no}^w}\lambda_{R_GP_{no}^w}$$

$$+K_{40}\lambda_{P_{no}^w}\lambda_{R_GM_{no}^w}\}+KK9(\lambda_{R_GP_{no}^d}-\lambda_{R_GP_{no}^w})=0 \qquad (XIII)$$

FIRST MOMENT

$$V\{K_7[R_G^w.][M^w]-K_{15}\lambda_{R_GP_{no}^w}\lambda_{R_GP_{n1}^w}+K_{11}[M^w]\lambda_{R_GP_{no}^w}$$

$$-(K_{16}+K_{22})\lambda_{P_{no}^w}\lambda_{R_GP_{n1}^w}-K_{35}[CCl_4^w]\lambda_{R_GP_{n1}^w}-K_{41}[M^w]\lambda_{R_GP_{n1}^w}$$

$$-K_{37}\lambda_{M_{no}^w}\lambda_{R_GP_{n1}^w}-K_{38}\lambda_{R_GM_{no}^w}\lambda_{R_GP_{n1}^w}+K_{38}\lambda_{R_GM_{n1}^w}\lambda_{R_GP_{no}^w}.$$

$$+K_{40}\lambda_{P_{no}^w}\lambda_{R_GM_{n1}^w}\}+KK9(\lambda_{R_GP_{n1}^d}-\lambda_{R_GP_{n1}^w})=0 \qquad (XIV)$$

SECOND MOMENT

$$V\{K_7[R_G^w.][M^w]+2K_{11}[M^w]\lambda_{R_GP_{n1}^w}+K_{11}\lambda_{R_GP_{no}^w}[M^w]$$

$$-K_{15}\lambda_{R_GP_{no}^w}\lambda_{R_GP_{n2}^w}-(K_{16}+K_{22})\lambda_{P_{no}^w}\lambda_{R_GP_{n2}^w}-K_{35}[CCl_4^w]\lambda_{R_GP_{n2}^w}$$

$$-K_{41}[M^w]\lambda_{R_GP_{n2}^w}-K_{37}\lambda_{M_{no}^w}\lambda_{R_GP_{n2}^w}-K_{38}\lambda_{R_GM_{no}^w}\lambda_{R_GP_{n2}^w}$$

$$+K_{38}\lambda_{R_GP_{no}^w}\lambda_{R_GM_{n2}^w}+K_{40}\lambda_{P_{no}^w}\lambda_{R_GM_{n2}^w}\}+KK9(\lambda_{R_GP_{n2}^d}-\lambda_{R_GP_{n2}^w})=0 \quad (XV)$$

TABLE 6

EQUATIONS USED IN SUBROUTINE NEWTON

ion (IV)

$$a_2 \lambda_{R_G P_{no}^d} + a_3 \lambda_{R_G P_{no}^d} \lambda_{P_{no}^d} + a_4 \lambda_{P_{no}^d} + a_6 \lambda_{P_{no}^d}^2 + a_5 \lambda_{P_{no}^w} = 0$$

,

$$a_2 = (1-V) \{K_{27}[CCl_4^d] + K_{29}[M^d] + K_{31} \lambda_{M_{no}^d} \}$$

$$a_3 = (1-V) \{-(K_{19} + K_{25})\}$$

$$a_4 = -(1-V) K_{34} \lambda_{R_G M_{no}^d} - KK10$$

$$a_5 = KK10$$

$$a_6 = (1-V) \{-(K_{20} + K_{26})\}$$

(IV) is a quadratic equation in $\lambda_{P_{no}^d}$

erentiating Eq.(IV) w.r.t. $\lambda_{P_{no}^w}$ and $\lambda_{R_G P_{no}^d}$

$$\frac{\partial (\lambda_{P_{no}^d})}{\partial \lambda_{P_{no}^w}} = \frac{-a_5}{(2a_6 + a_4 + a_3 \lambda_{R_G P_{no}^d})} \qquad \text{IV(A)}$$

$$\frac{\partial (\lambda_{P_{no}^d})}{\partial \lambda_{R_G P_{no}^d}} = \frac{-(a_2 + a_3 \lambda_{P_{no}^d})}{(a_4 + 2a_6 + a_3 \lambda_{R_G P_{no}^d})} \qquad \text{IV(B)}$$

ion (XIII)

$$r_1 \lambda_{R_G P_{no}^w}^2 + r_2 \lambda_{P_{no}^w} \lambda_{R_G P_{no}^w} + r_3 \lambda_{R_G P_{no}^w} + \{r_4 + KK9 \lambda_{R_G P_{no}^d}\} = 0$$

$$r_1 = (-VK_{15})$$

$$r_2 = V \{-(K_{16} + K_{22})\}$$

$$r_3 = -KK9 + V\{-K_{35}[CCl_4^d] - K_{41}[M^w] - K_{37} \lambda_{M_{no}^w}\}$$

$$r_4 = V\{K_7[R_G^w \cdot][M^w] + K_{40} \lambda_{P_{no}^w} \lambda_{R_G P_{no}^w}\}$$

. (XIII) is a quadratic equation in $\lambda_{R_G P_{no}^w}$

Differentiate eqn.(XII) w.r.t. $\lambda_{P_{no}^w}$ and $\lambda_{R_G P_{no}^d}$

$$\frac{\partial(\lambda_{R_G P_{no}^w})}{\partial\lambda_{P_{no}^w}} = \frac{-(r_4 + r_2\lambda_{R_G P_{no}^w})}{(2r_1 + r_3)} \qquad \text{XIII(A)}$$

$$\frac{\partial(\lambda_{R_G P_{no}^w})}{\partial\lambda_{R_G P_{no}^d}} = \frac{KK9}{(2r_1 + r_2\lambda_{P_{no}^w} + r_3)} \qquad \text{XIII(B)}$$

Functions to be iterated upon:

Equation (VII)

$$F(\lambda_{R_G P_{no}^d}) = b_2\lambda_{R_G P_{no}^d} + a_3\lambda_{R_G P_{no}^d}\lambda_{P_{no}^d} + b_4\lambda_{P_{no}^d}$$

$$+ b_5\lambda_{R_G P_{no}^w} + b_6\lambda_{R_G P_{no}^d}^2$$

where,

$$b_2 = (1-V)\{-K_{27}[CCl_4^d] - K_{29}[M^d] - K_{31}\lambda_{M_{no}^d}\} - KK9$$

$$b_3 = (1-V)\{-(K_{19} + K_{25})\}$$

$$b_4 = (1-V)\{K_{34}\lambda_{R_G M_{no}^d}\}$$

$$b_5 = KK3$$

$$b_6 = (1-V)K_{18}$$

Differentiating eqn.(VII) w.r.t. $\lambda_{P_{no}^w}$ and $\lambda_{R_G P_{no}^d}$

$$\frac{\partial[F(\lambda_{R_G P_{no}^d})]}{\partial\lambda_{P_{no}^w}} = (a_3\lambda_{R_G P_{no}^d} + b_4)\frac{\partial(\lambda_{P_{no}^d})}{\partial\lambda_{P_{no}^w}} + b_5\frac{\partial(\lambda_{R_G P_{no}^w})}{\partial\lambda_{P_{no}^w}}$$

$$\frac{\partial[F(\lambda_{R_G P_{no}^d})]}{\partial\lambda_{R_G P_{no}^d}} = (b_2 + a_3\lambda_{P_{no}^d} + 2b_6) + (a_3\lambda_{R_G P_{no}^d} + b_4)\frac{\partial(\lambda_{P_{no}^d})}{\partial\lambda_{R_G P_{no}^d}}$$

$$+ b_5\frac{\partial(\lambda_{R_G P_{no}^w})}{\partial\lambda_{R_G P_{no}^d}} \qquad \text{VII(B)}$$

Equation (X)

$$F(\lambda_{P_{no}}^W) = V\{K_3[CCl_4^W][OH_c^W] + K_{35}[CCl_4^W]\lambda_{R_GP_{no}^W}$$

$$-(K_{16}+K_{22})\lambda_{R_GP_{no}^W}\lambda_{P_{no}^W} - (K_{17}+K_{23})\lambda_{P_{no}^W}^2 + K_{37}\lambda_{M_{no}^W}\lambda_{R_GP_{no}^W}$$

$$-K_{40}\lambda_{R_GM_{no}^W}\lambda_{P_{no}^W} + K_{41}[M^W]\lambda_{R_GP_{no}^W} + KK10(\lambda_{P_{no}}^d - \lambda_{P_{no}}^W)$$

Differentiating eqn.(X) w.r.t. $\lambda_{P_{no}^W}$ and $\lambda_{R_GP_{no}^d}$

$$\frac{\partial[F(\lambda_{P_{no}^W})]}{\partial\lambda_{P_{no}^W}} = V\{K_{35}[CCl_4^W] - (K_{16}+K_{22})\lambda_{P_{no}^W} + K_{37}\lambda_{M_{no}^W}$$

$$+K_{41}[M^W]\} \frac{\partial(\lambda_{R_GP_{no}^W})}{\partial\lambda_{P_{no}^W}} + V\{-(K_{16}+K_{22})\lambda_{R_GP_{no}^W}$$

$$-2(K_{17}+K_{23})\lambda_{P_{no}^W} - K_{40}\lambda_{R_GM_{no}^W}\} - KK10 + KK10\frac{\partial(\lambda_{P_{no}}^d)}{\partial\lambda_{P_{no}^W}}$$

$$X(A)$$

$$\frac{\partial[F(\lambda_{P_{no}^W})]}{\partial\lambda_{R_GP_{no}^d}} = V\{K_{35}[CCl_4^W] - (K_{16}+K_{22})\lambda_{P_{no}^W} + K_{37}\lambda_{M_{no}^W}$$

$$+K_{41}[M^W]\} \frac{d(\lambda_{R_GP_{no}^W})}{d\lambda_{R_GP_{no}^d}} + KK10\frac{\partial(\lambda_{P_{no}}^d)}{\partial\lambda_{R_GP_{no}^d}} \quad X(B)$$

TABLE 7

DERIVATION OF MOMENT EQUATIONS (6),(7) and (8) FROM EQUATION (A)

Mole balance for nth particle of dead homopolymer in the aqueous phase (M_n^W)

FROM TABLE 3

$$\frac{d[M_n^W]}{dt} = V\{K_{16}[P_n^W][\sum_{r=1}^{\infty} R_G P_r^W]+K_{17}[P_n^W][\sum_{r=1}^{\infty} P_r^W]+K_{23}\sum_{r=1}^{n-1}[P_r^W][P_{n-r}^W]$$

$$+K_{36}[P_n^W][CCl_4^W]+K_{42}[P_n^W][M^W]-K_{37}[M_n^W][\sum_{r=1}^{\infty} R_G P_r^W]$$

$$+K_{40}[P_n^W][\sum_{r=1}^{\infty} R_G M_r^W]+K_{39}[P_n^W][\sum_{r=1}^{\infty} M_r^W]-K_{39}[M_n^W][\sum_{r=1}^{\infty} P_r^W]\}$$

$$+KK49\{[M_n^d]-[M_n^W]\} \qquad\qquad (A)$$

(i) Summing up over all particles from n=1 to n=∞

$$\frac{d}{dt}[\sum_{r=1}^{\infty} M_n^W] = V\{K_{16}[\sum_{n=1}^{\infty} P_n^W][\sum_{r=1}^{\infty} R_G P_r^W] + K_{17}[\sum_{n=1}^{\infty} P_n^W][\sum_{r=1}^{\infty} P_r^W]$$

$$+K_{23}\sum_{n=1}^{\infty}\sum_{r=1}^{n-1}[P_r^W][P_{n-r}^W]+K_{36}[\sum_{n=1}^{\infty} P_n^W][CCl_4^W]$$

$$+K_{42}[\sum_{n=1}^{\infty} P_n^W][M^W]+K_{40}[\sum_{n=1}^{\infty} P_n^W][\sum_{r=1}^{\infty} R_G M_r^W]$$

$$+K_{39}[\sum_{n=1}^{\infty} P_n^W][\sum_{r=1}^{\infty} M_r^W]-K_{37}[\sum_{n=1}^{\infty} M_n^W][\sum_{r=1}^{\infty} R_G P_r^W]$$

$$-K_{39}[\sum_{n=1}^{\infty} M_n^W][\sum_{r=1}^{\infty} P_r^W]\}+KK49\{[\sum_{n=1}^{\infty} M_n^d]-[\sum_{n=1}^{\infty} M_n^W]\}$$

i.e., $\frac{d}{dt}(\lambda_{M_{no}^W}) = V\{K_{16}\lambda_{P_{no}^W}\lambda_{R_G P_{no}^W} + K_{17}\lambda^2_{P_{no}^W} + K_{23}[\sum\limits_{n=1}^{\infty} P_n^W][\sum\limits_{r=1}^{\infty} P_r^W]$

$\qquad\qquad +K_{36}\lambda_{P_{no}^W}[CCl_4^W] + K_{42}\lambda_{P_{no}^W}[M^W] - K_{37}\lambda_{M_{no}^W}\lambda_{R_G P_{no}^W}$

$\qquad\qquad +K_{40}\lambda_{P_{no}^W}\lambda_{R_G M_{no}^W} + K_{39}\lambda_{P_{no}^W}\lambda_{M_{no}^W} - K_{39}\lambda_{P_{no}^W}\lambda_{M_{no}^W}\}$

$\qquad\qquad +KK49(\lambda_{M_{no}^d} - \lambda_{M_{no}^W})$

$\left[\because \sum\limits_{n=1}^{\infty} n^o \sum\limits_{r=1}^{n-1}[P_r^W][P_{n-r}^W] = \sum\limits_{n=1}^{\infty}\sum\limits_{r=1}^{\infty}[P_n^W][P_r^W] = [\sum\limits_{r=1}^{\infty} P_r^W][\sum\limits_{n=1}^{\infty} P_n^W] \right]$

and by definition of zeroth moment

i.e., $\frac{d}{dt}(\lambda_{M_{no}^W}) = V\{K_{16}\lambda_{P_{no}^W}\lambda_{R_G P_{no}^W} + (K_{17}+K_{23})\lambda^2_{P_{no}^W} + K_{40}\lambda_{P_{no}^W}\lambda_{R_G M_{no}^W}$

$\qquad\qquad +K_{36}\lambda_{P_{no}^W}[CCl_4^W] + K_{42}\lambda_{P_{no}^W}[M^W] - K_{37}\lambda_{M_{no}^W}\lambda_{R_G P_{no}^W}$

$\qquad\qquad +K_{40}\lambda_{P_{no}^W}\lambda_{R_G M_{no}^W} + KK49(\lambda_{M_{no}^d} - \lambda_{M_{no}^W})$ (6)

(ZEROTH MOMENT EQUATION)

(ii) Multiplying equation (A) on both sides by n and summing up over all particles from n=1 to n=∞

$\frac{d}{dt}[\sum\limits_{n=1}^{\infty} n M_n^W] = V(K_{16}[\sum\limits_{n=1}^{\infty} n P_n^W][\sum\limits_{r=1}^{\infty} R_G P_r^W] + K_{17}[\sum\limits_{n=1}^{\infty} n P_n^W][\sum\limits_{r=1}^{\infty} P_r^W]$

$\qquad\qquad +K_{23}\sum\limits_{n=1}^{\infty} n\sum\limits_{r=1}^{n-1}[P_r^W][P_{n-r}^W] + K_{36}[\sum\limits_{n=1}^{\infty} n P_n^W][CCl_4^W]$

$\qquad\qquad +K_{42}[\sum\limits_{n=1}^{\infty} n P_n^W][M^W] - K_{37}[\sum\limits_{n=1}^{\infty} n M_n^W][\sum\limits_{r=1}^{\infty} R_G P_r^W]$

$\qquad\qquad +K_{40}[\sum\limits_{n=1}^{\infty} n P_n^W][\sum\limits_{r=1}^{\infty} R_G M_r^W] + K_{39}[\sum\limits_{n=1}^{\infty} n P_n^W][\sum\limits_{r=1}^{\infty} M_r^W]$

$\qquad\qquad -K_{39}[\sum\limits_{n=1}^{\infty} n M_n^W][\sum\limits_{r=1}^{\infty} P_r^W]\} + KK49\{[\sum\limits_{n=1}^{\infty} n M_n^d] - [\sum\limits_{n=1}^{\infty} n M_n^W]\}$

i.e., $\dfrac{d}{dt}[\sum\limits_{n=1}^{\infty} nM_n^W] = V(K_{16}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} R_G P_r^W] + K_{17}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} P_r^W]$

$$+K_{23}\sum\limits_{n=1}^{\infty}\sum\limits_{r=1}^{\infty}(n+r)[P_r^W][P_n^W]+K_{36}[\sum\limits_{n=1}^{\infty} nP_n^W][CCl_4^W]$$

$$+K_{42}[\sum\limits_{n=1}^{\infty} nP_n^W][M^W]-K_{37}[\sum\limits_{n=1}^{\infty} nM_n^W][\sum\limits_{r=1}^{\infty} R_G P_r^W]$$

$$+K_{40}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} R_G M_r^W]+K_{39}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} M_r^W]$$

$$-K_{39}[\sum\limits_{n=1}^{\infty} nM_n^W][\sum\limits_{r=1}^{\infty} P_r^W]\}+KK49\{[\sum\limits_{n=1}^{\infty} nM_n^d]-[\sum\limits_{n=1}^{\infty} nM_n^W]\}$$

$$\left[\therefore\ \sum\limits_{n=1}^{\infty} n\sum\limits_{r=1}^{n-1}[P_n^W][P_{n-r}^W] = \sum\limits_{n=1}^{\infty}\sum\limits_{r=1}^{\infty}(n+r)[P_n^W][P_r^W]\right]$$

i.e., $\dfrac{d}{dt}[\sum\limits_{n=1}^{\infty} nM_n^W] = V\{K_{16}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} R_G P_r^W] + K_{17}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} P_r^W]$

$$+K_{23}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} P_r^W]+K_{23}[\sum\limits_{n=1}^{\infty} P_n^W][\sum\limits_{r=1}^{\infty} rP_r^W]$$

$$+K_{36}[CCl_4^W]\ [\sum\limits_{n=1}^{\infty} nP_n^W]+K_{42}[\sum\limits_{n=1}^{\infty} nP_n^W][M^W]$$

$$-K_{37}[\sum\limits_{n=1}^{\infty} nM_n^W][\sum\limits_{r=1}^{\infty} R_G P_r^W]+K_{40}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} R_G M_r^W]$$

$$+K_{39}[\sum\limits_{n=1}^{\infty} nP_n^W][\sum\limits_{r=1}^{\infty} M_r^W]-K_{39}[\sum\limits_{n=1}^{\infty} nM_n^W][\sum\limits_{r=1}^{\infty} P_r^W]\}$$

$$+KK49\{[\sum\limits_{n=1}^{\infty} nM_n^d]-[\sum\limits_{n=1}^{\infty} nM_n^W]\}$$

$\dfrac{d}{dt}(\lambda_{M_{n1}^W}) = V\{K_{16}\lambda_{R_G P_{no}^W}\lambda_{P_{n1}^W} + K_{17}\lambda_{P_{no}^W}\lambda_{P_{n1}^W}+2K_{23}\lambda_{P_{no}^W}\lambda_{P_{n1}^W}$

$$+K_{36}[CCl_4^W]\lambda_{P_{n1}^W}+K_{42}[M^W]\lambda_{P_{n1}^W}-K_{37}\lambda_{R_G P_{no}^W}\lambda_{M_{n1}^W}$$

$$+K_{40}\lambda_{R_G M_{no}^W}\lambda_{P_{n1}^W}+K_{39}\lambda_{M_{no}^W}\lambda_{P_{n1}^W}-K_{39}\lambda_{P_{no}^W}\lambda_{M_{n1}^W}\}$$

$$+KK49(\lambda_{M_{n1}^d}-\lambda_{M_{n1}^W}) \tag{7}$$

(FIRST MOMENT EQUATION)

[by definition of first and zeroth moments]

(iii) Multiplying both sides of Equation (A) by n^2 and summing up over all particles from $n=1$ to $n=\infty$

$$\frac{d}{dt}[\sum_{n=1}^{\infty} n^2 M_n^W] = V(K_{16}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} R_G P_r^W] + K_{17}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} P_r^W]$$

$$+ K_{23}\sum_{n=1}^{\infty} n^2 \sum_{r=1}^{n-1}[P_r^W][P_{n-r}^W] + K_{36}[\sum_{r=1}^{\infty} n^2 P_n^W][CCl_4^W]$$

$$+ K_{42}[\sum_{n=1}^{\infty} n^2 P_n^W][M^W] - K_{37}[\sum_{n=1}^{\infty} n^2 M_n^W][\sum_{r=1}^{\infty} R_G P_r^W]$$

$$+ K_{40}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} R_G M_r^W] + K_{39}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} M_r^W]$$

$$- K_{39}[\sum_{n=1}^{\infty} n^2 M_n^W][\sum_{r=1}^{\infty} P_r^W]\} + KK49\{[\sum_{n=1}^{\infty} n^2 M_n^d] - [\sum_{n=1}^{\infty} n^2 M_n^W]\}$$

i.e., $$\frac{d}{dt}[\sum_{n=1}^{\infty} n^2 M_n^W] = V(K_{16}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} R_G P_r^W] + K_{17}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} P_r^W]$$

$$+ K_{23}\sum_{n=1}^{\infty} \sum_{r=1}^{n-1}(n+r)^2[P_r^W][P_n^W] + K_{36}[\sum_{n=1}^{\infty} n^2 P_n^W][CCl_4^W]$$

$$+ K_{42}[\sum_{n=1}^{\infty} n^2 P_n^W][M^W] - K_{37}[\sum_{n=1}^{\infty} n^2 M_n^W][\sum_{r=1}^{\infty} R_G P_r^W]$$

$$+ K_{40}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} R_G M_r^W] + K_{39}[\sum_{n=1}^{\infty} n^2 P_n^W][\sum_{r=1}^{\infty} M_r^W]$$

$$- K_{39}[\sum_{n=1}^{\infty} n^2 M_n^W][\sum_{r=1}^{\infty} P_r^W]\} + KK49\{[\sum_{n=1}^{\infty} n^2 M_n^d] - [\sum_{n=1}^{\infty} n^2 M_n^W]\}$$

$$\left[\because \sum_{n=1}^{\infty} n^2 \sum_{r=1}^{n-1}[P_n^W][P_{n-r}^W] = \sum_{n=1}^{\infty} \sum_{r=1}^{\infty}(n+r)^2[P_n^W][P_r^W]\right]$$

i.e., $\dfrac{d}{dt} \sum_{n=1} n^2 M_n^w = V\{K_{16}[\sum_{n=1}^{\infty} n^2 P_n^w][\sum_{r=1}^{\infty} R_G P_r^w] + K_{17}[\sum_{n=1}^{\infty} n^2 P_n^w][\sum_{r=1}^{\infty} P_r^w]$

$+ K_{23}[\sum_{n=1}^{\infty} n^2 P_n^w][\sum_{r=1}^{\infty} P_r^w] + 2K_{23}[\sum_{n=1}^{\infty} n P_n^w][\sum_{r=1}^{\infty} r P_r^w]$

$+ K_{23}[\sum_{n=1}^{\infty} P_n^w][\sum_{r=1}^{\infty} r P_r^w] + K_{36}[\sum_{n=1}^{\infty} n^2 P_n^w][CCl_4^w]$

$+ K_{42}[\sum_{n=1}^{\infty} n^2 P_n^w][M^w] - K_{37}[\sum_{n=1}^{\infty} n^2 M_n^w][\sum_{r=1}^{\infty} R_G P_r^w]$

$+ K_{40}[\sum_{n=1}^{\infty} n^2 P_n^w][\sum_{r=1}^{\infty} R_G M_r^w] + K_{39}[\sum_{n=1}^{\infty} n^2 P_n^w][\sum_{r=1}^{\infty} M_r^w]$

$- K_{39}[\sum_{n=1}^{\infty} n^2 M_n^w][\sum_{r=1}^{\infty} P_r^w]\} + KK49\{[\sum_{n=1}^{\infty} n^2 M_n^d] - [\sum_{n=1}^{\infty} n^2 M_n^w]\}$

$\dfrac{d}{dt}(\lambda_{M_{n2}^w}) = V\{K_{16}\lambda_{R_G P_{no}^w}\lambda_{P_{n2}^w} + K_{17}\lambda_{P_{no}^w}\lambda_{P_{n2}^w} + 2K_{23}\lambda_{P_{no}^w}\lambda_{P_{n2}^w}$

$+ 2K_{23}\lambda_{P_{n1}^w}^2 + K_{36}\lambda_{P_{n2}^w}[CCl_4^w] + K_{42}[M^w]\lambda_{P_{n2}^w}$

$- K_{37}\lambda_{R_G P_{no}^w}\lambda_{M_{n2}^w} + K_{40}\lambda_{R_G M_{no}^w}\lambda_{P_{n2}^w} + K_{39}\lambda_{M_{no}^w}\lambda_{P_{n2}^w}$

$- K_{39}\lambda_{P_{no}^w}\lambda_{M_{n2}^w}\} + KK49(\lambda_{M_{n2}^d} - \lambda_{M_{n2}^w})$ \hfill (8)

(By definition of zeroth, first and second moments)

(SECOND MOMENT EQUATION)
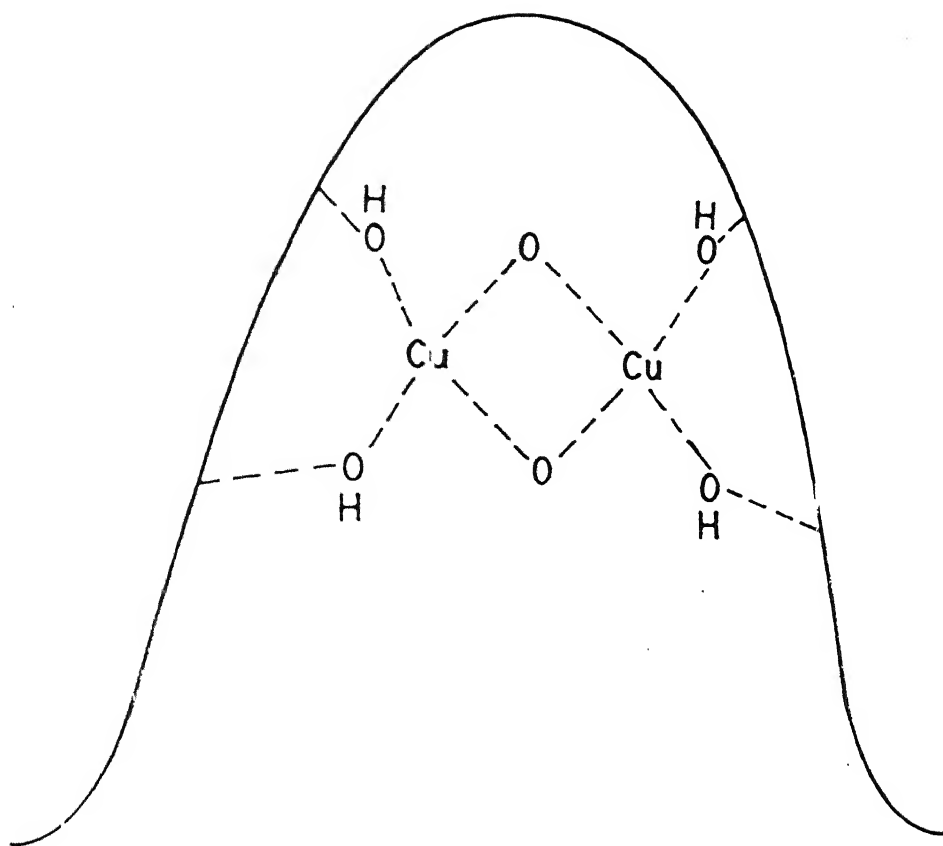
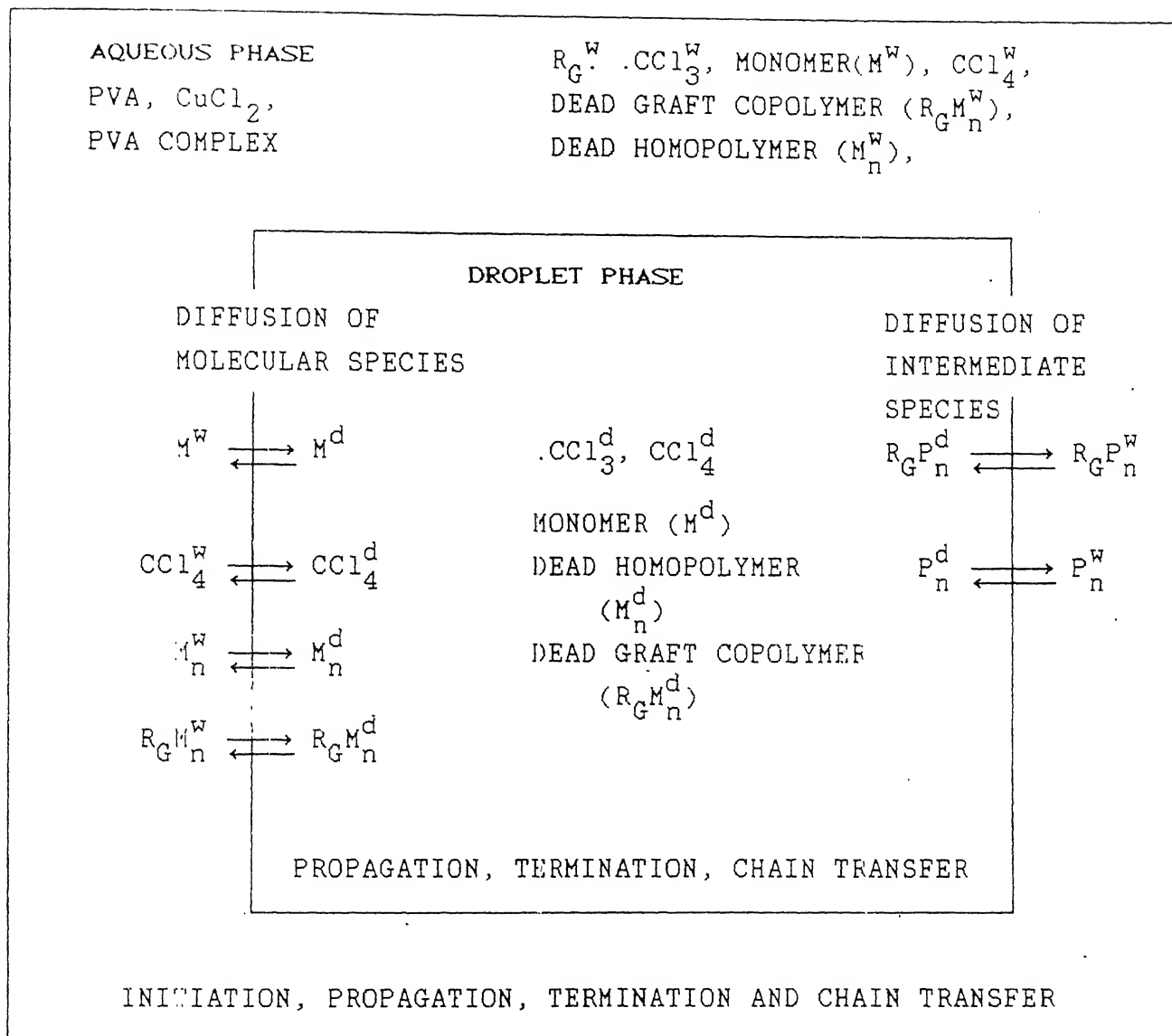FIG. 1   PVA-COPPER (II) COMPLEX STRUCTURE [18]

FIG. 2   EXPERIMENTAL SETUP

AQUEOUS PHASE

PVA, $CuCl_2$,

PVA COMPLEX

R_G^W . CCl_3^W, MONOMER(M^W), CCl_4^W,

DEAD GRAFT COPOLYMER ($R_G M_n^W$),

DEAD HOMOPOLYMER (M_n^W),

DROPLET PHASE

DIFFUSION OF MOLECULAR SPECIES

DIFFUSION OF INTERMEDIATE SPECIES

$M^W \rightleftarrows M^d$

.CCl_3^d, CCl_4^d

$R_G P_n^d \rightleftarrows R_G P_n^W$

MONOMER (M^d)

$CCl_4^W \rightleftarrows CCl_4^d$

DEAD HOMOPOLYMER (M_n^d)

$P_n^d \rightleftarrows P_n^W$

$M_n^W \rightleftarrows M_n^d$

DEAD GRAFT COPOLYMER ($R_G M_n^d$)

$R_G M_n^W \rightleftarrows R_G M_n^d$

PROPAGATION, TERMINATION, CHAIN TRANSFER

INITIATION, PROPAGATION, TERMINATION AND CHAIN TRANSFER

FIGURE 3: SCHEMATIC REPRESENTATION OF THE REACTION MASS

Temp. °C	Reaction system	pH
□ 80	PVA-Styrene	10.18
△ 70	PVA-MMA	9.26
○ 80	PVA-MMA	10.1
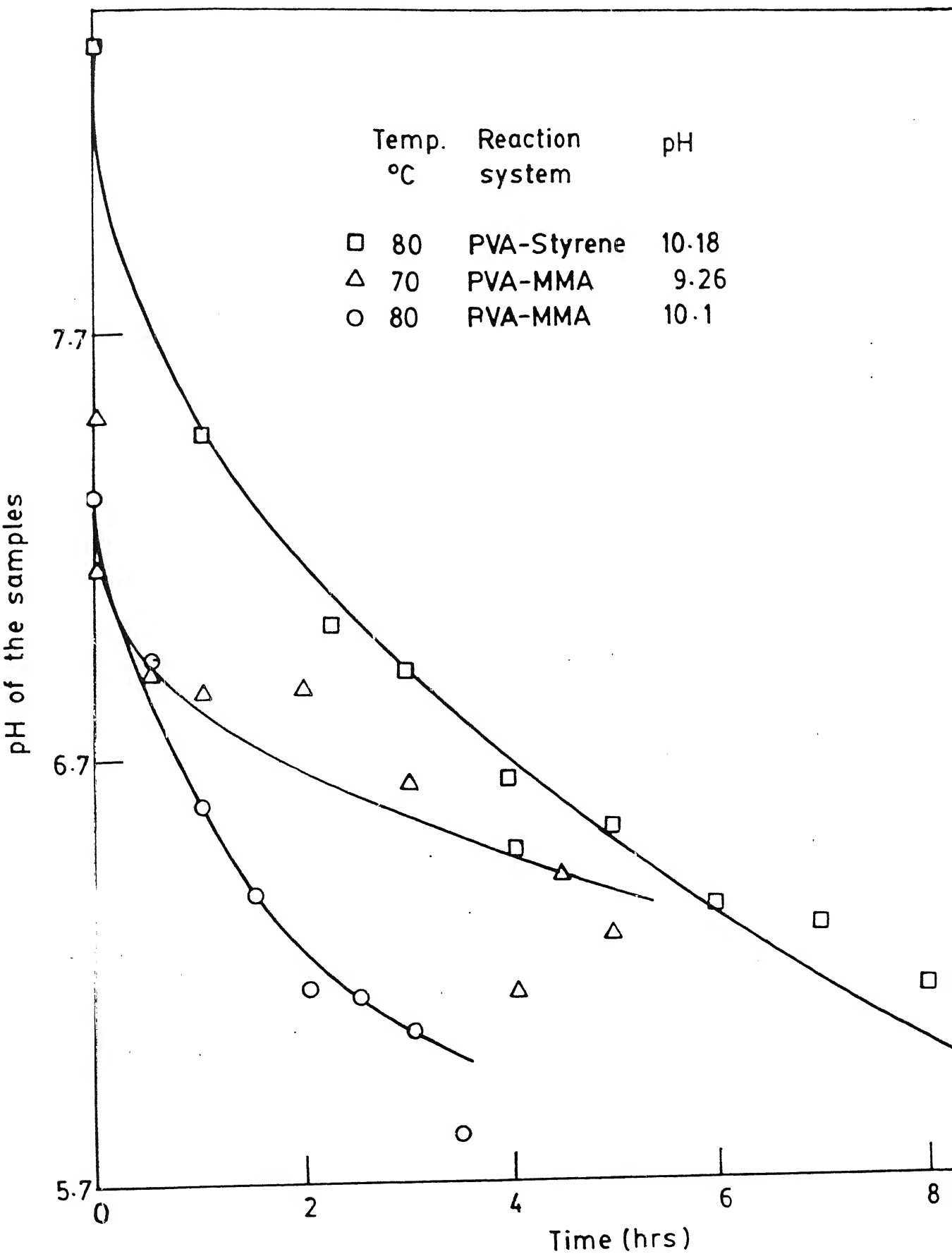
FIG. 4   VARIATION OF pH OF THE REACTION MASS WITH TIME
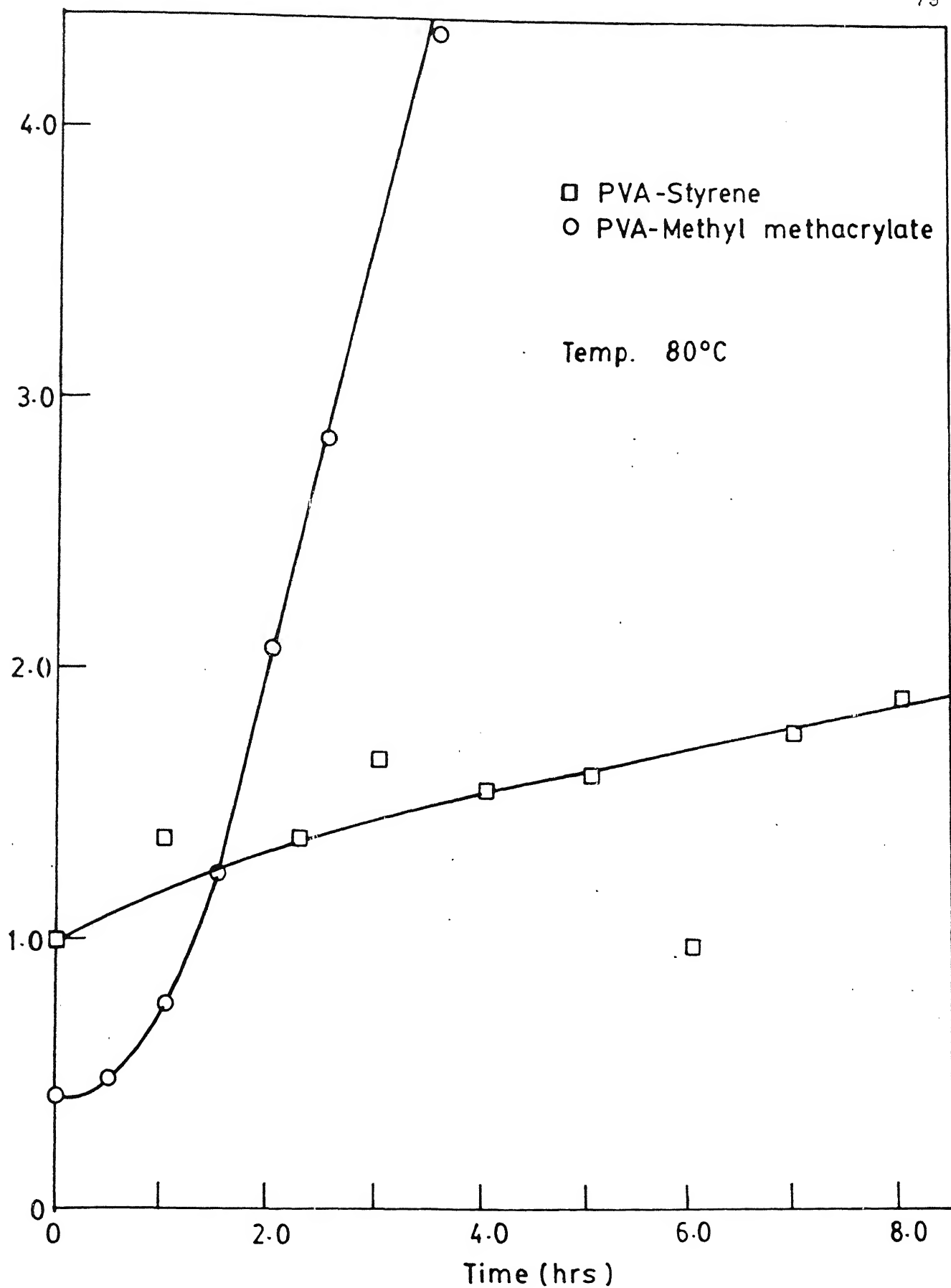
FIG 5   WEIGHT OF DRIED SAMPLES (GM) VS TIME (HRS)
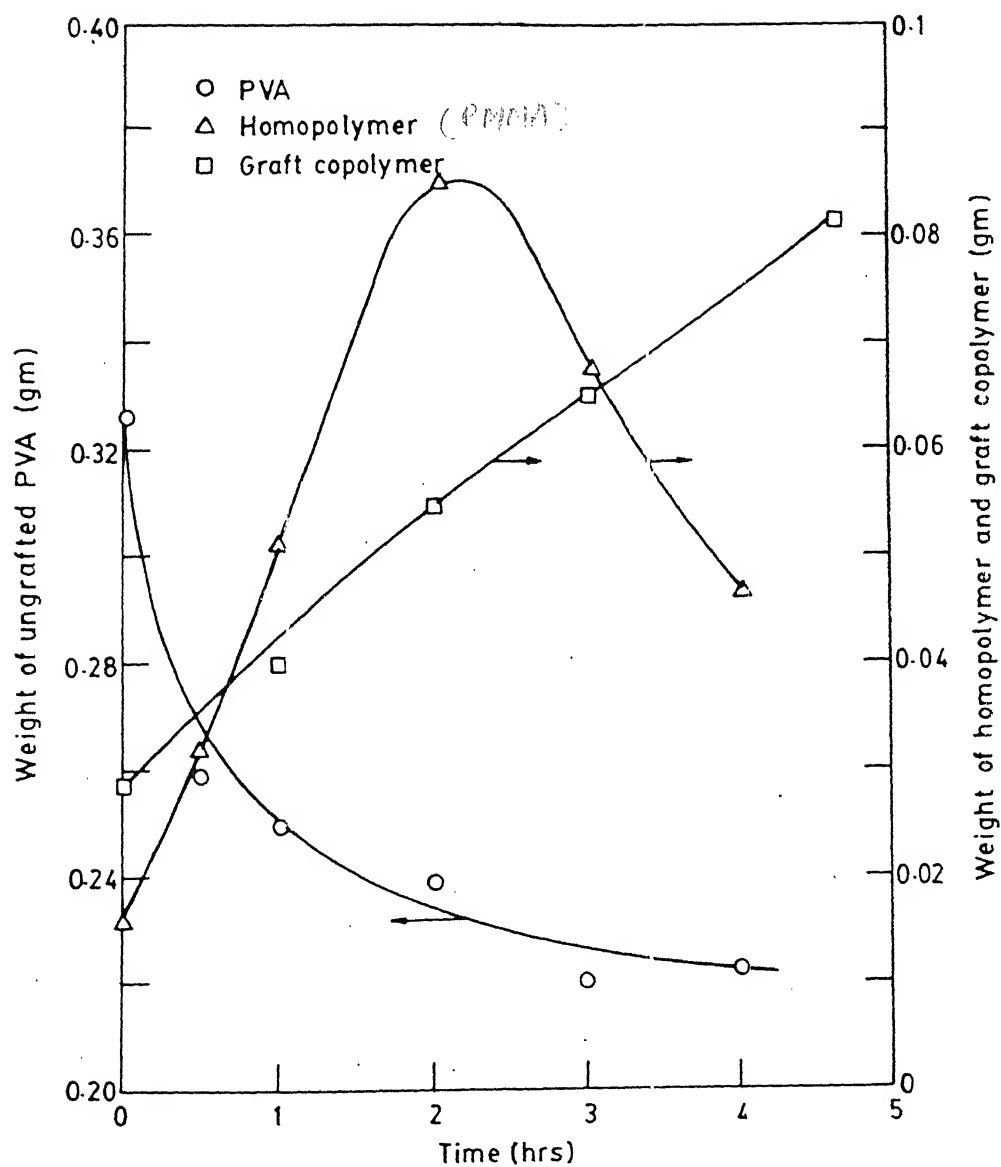
FIG.6   AMOUNT OF COMPONENTS FORMED (gm) VS. TIME (hrs)
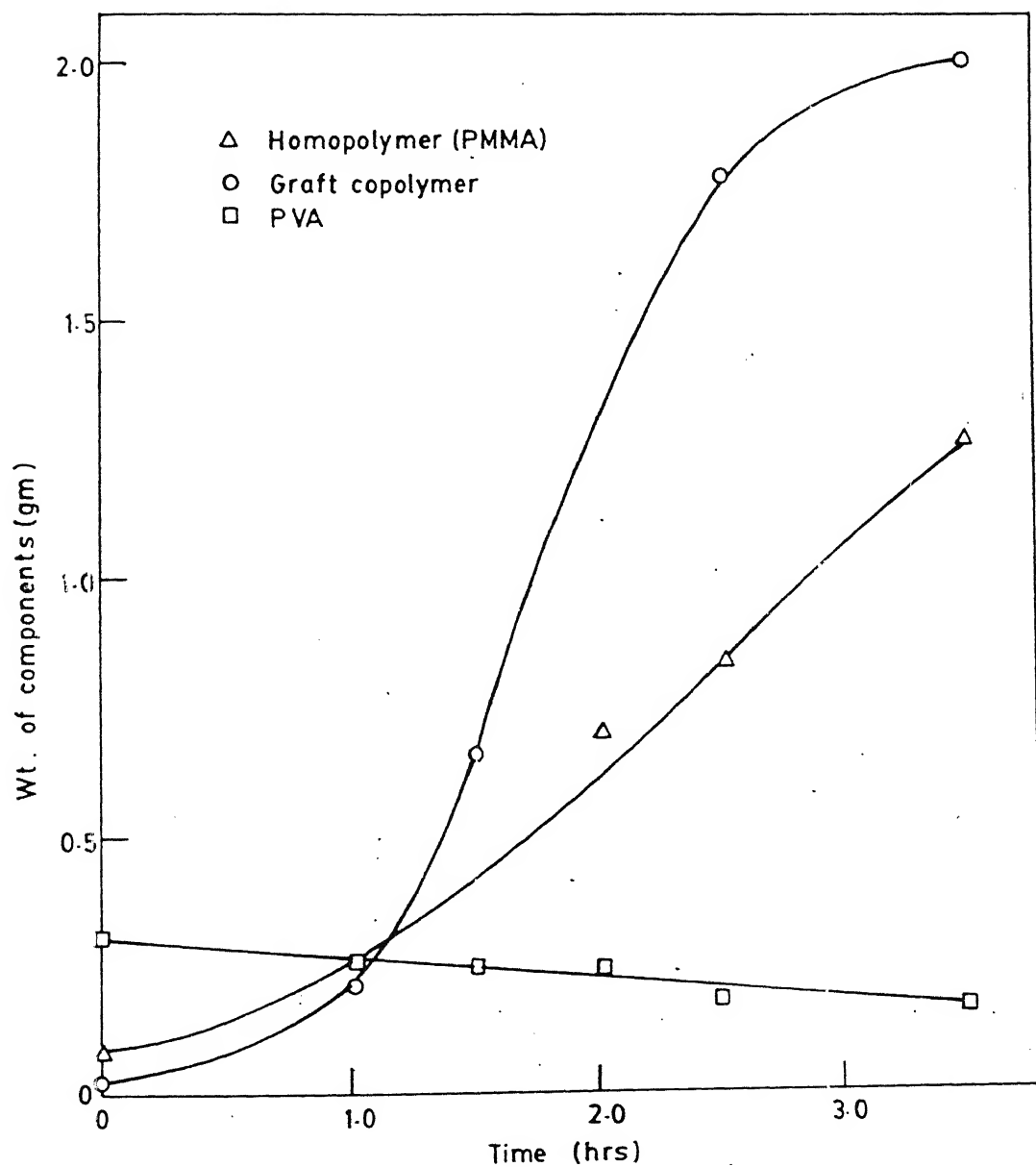
FIG. 7   WEIGHT OF COMPONENTS (gm) VS. TIME (hrs)
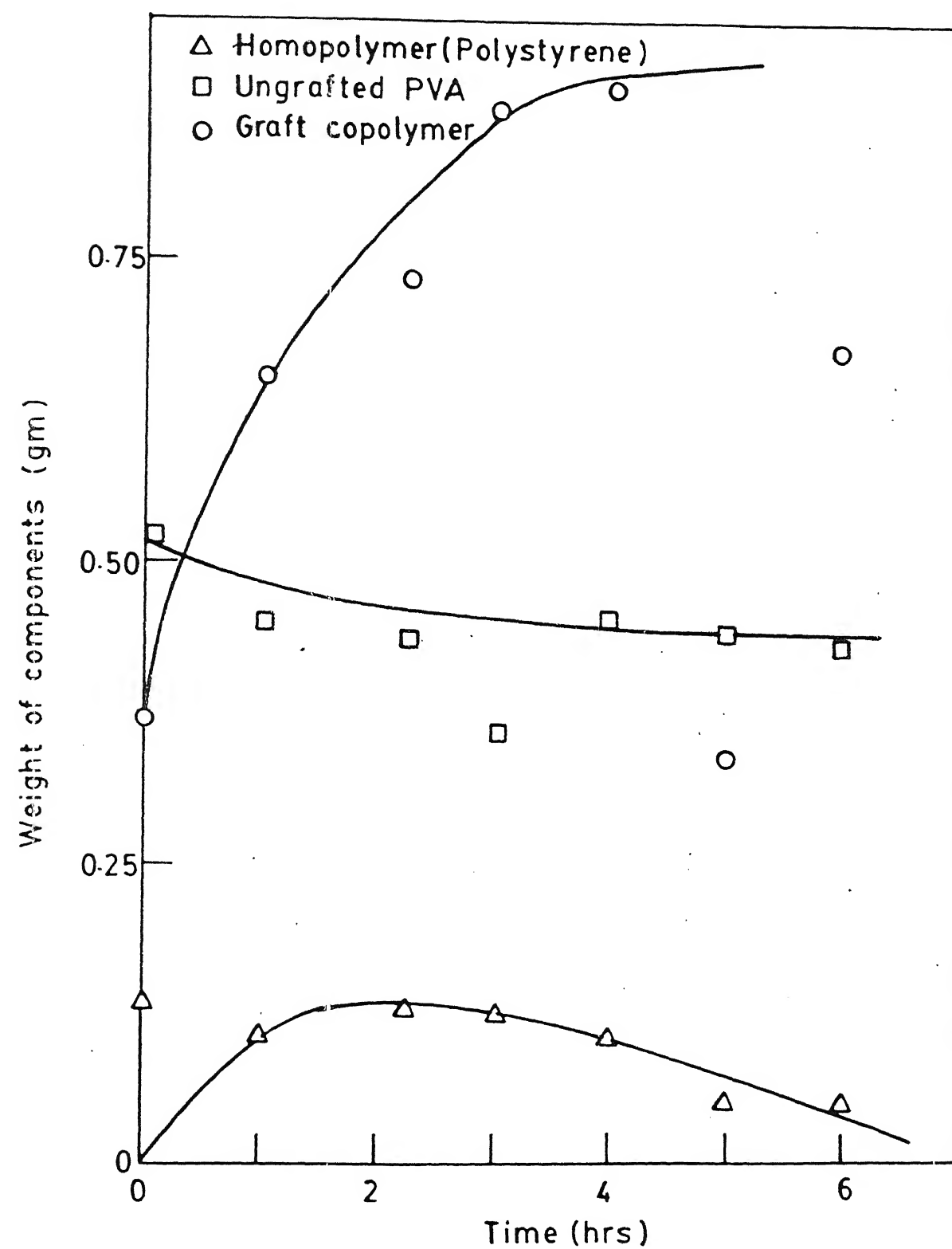
FIG. 8   WEIGHT OF COMPONENTS FORMED (gm) VS. TIME (h
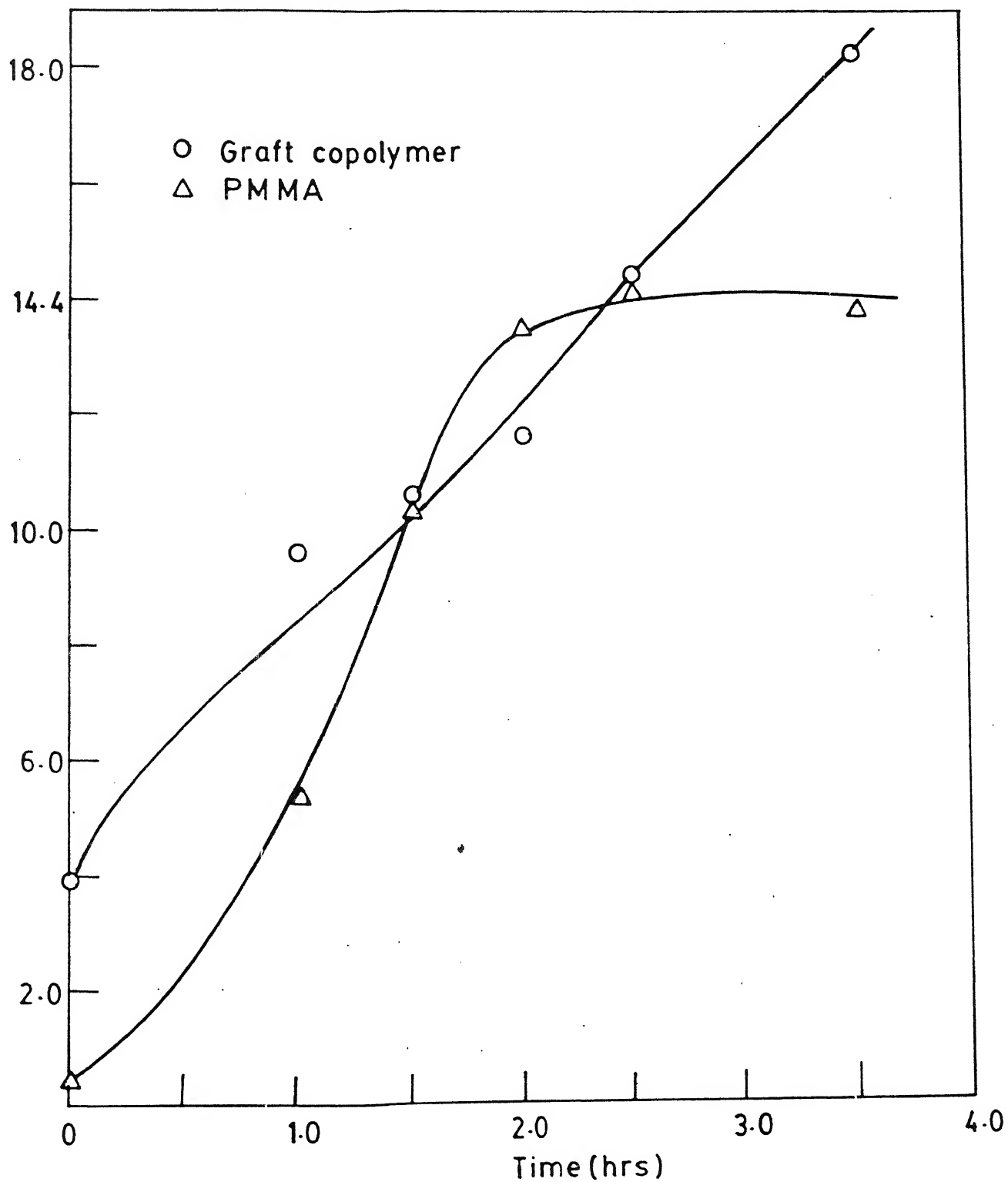
FIG. 9   MOLECULAR WEIGHT OF GRAFT COPOLYMER AND HOMO-
POLYMER VS. TIME (HRS)
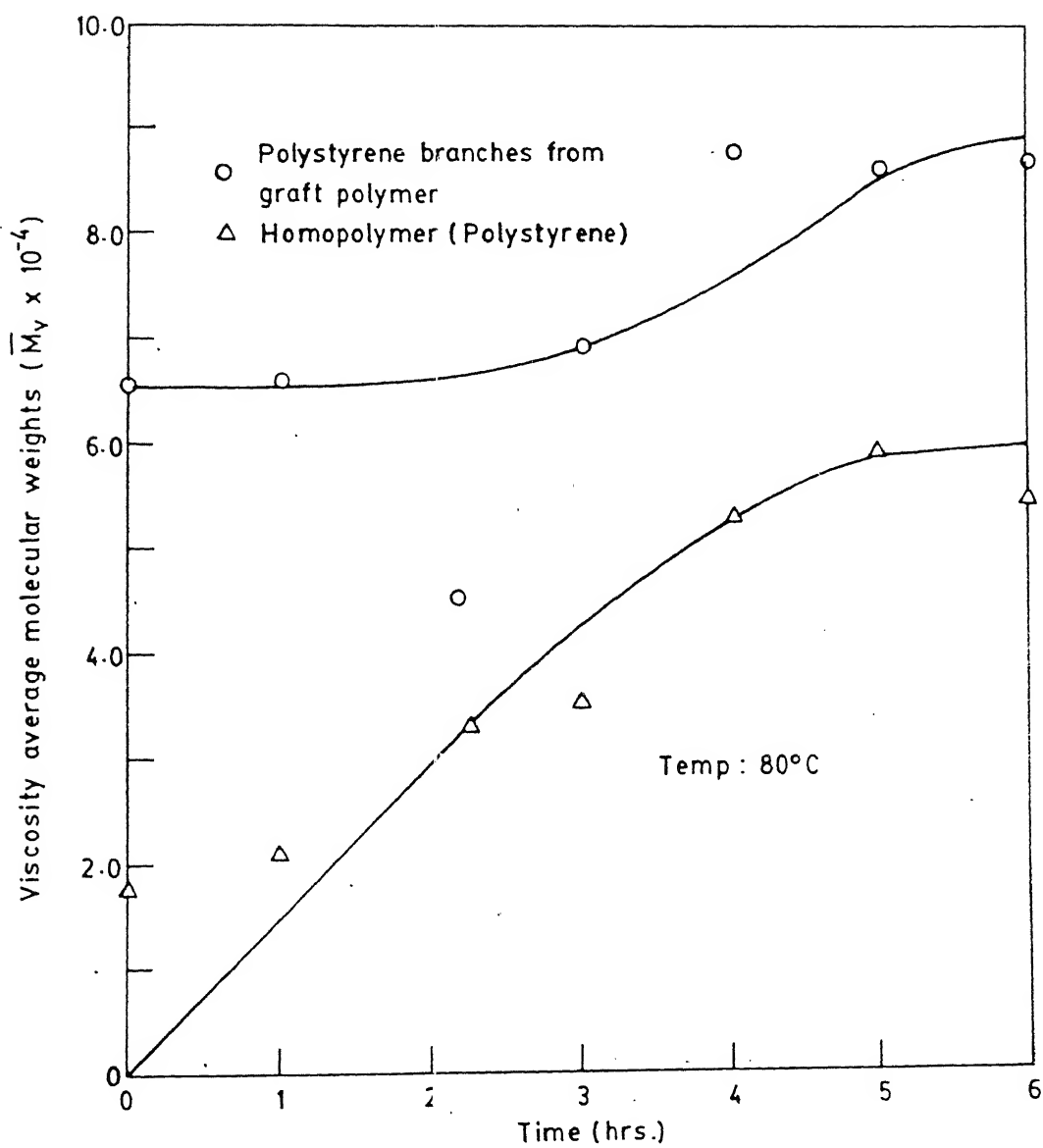
FIG. 10   MOLECULAR WEIGHTS OF HOMOPOLYMER AND GRAFT COPOLY-
MER VS. TIME
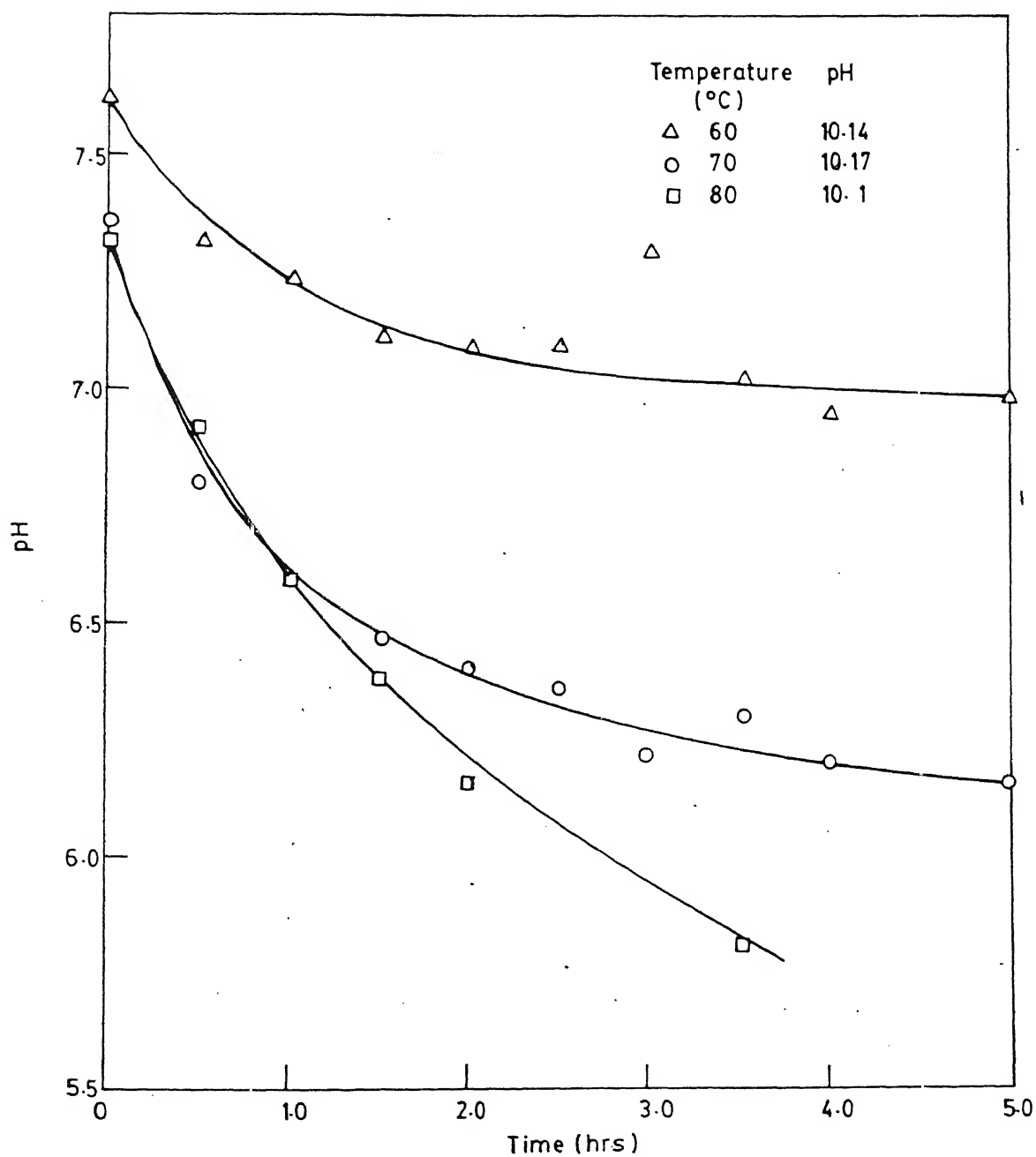
FIG. 11   EFFECT OF TEMPERATURE: VARIATION OF pH WITH TIME (Hrs)
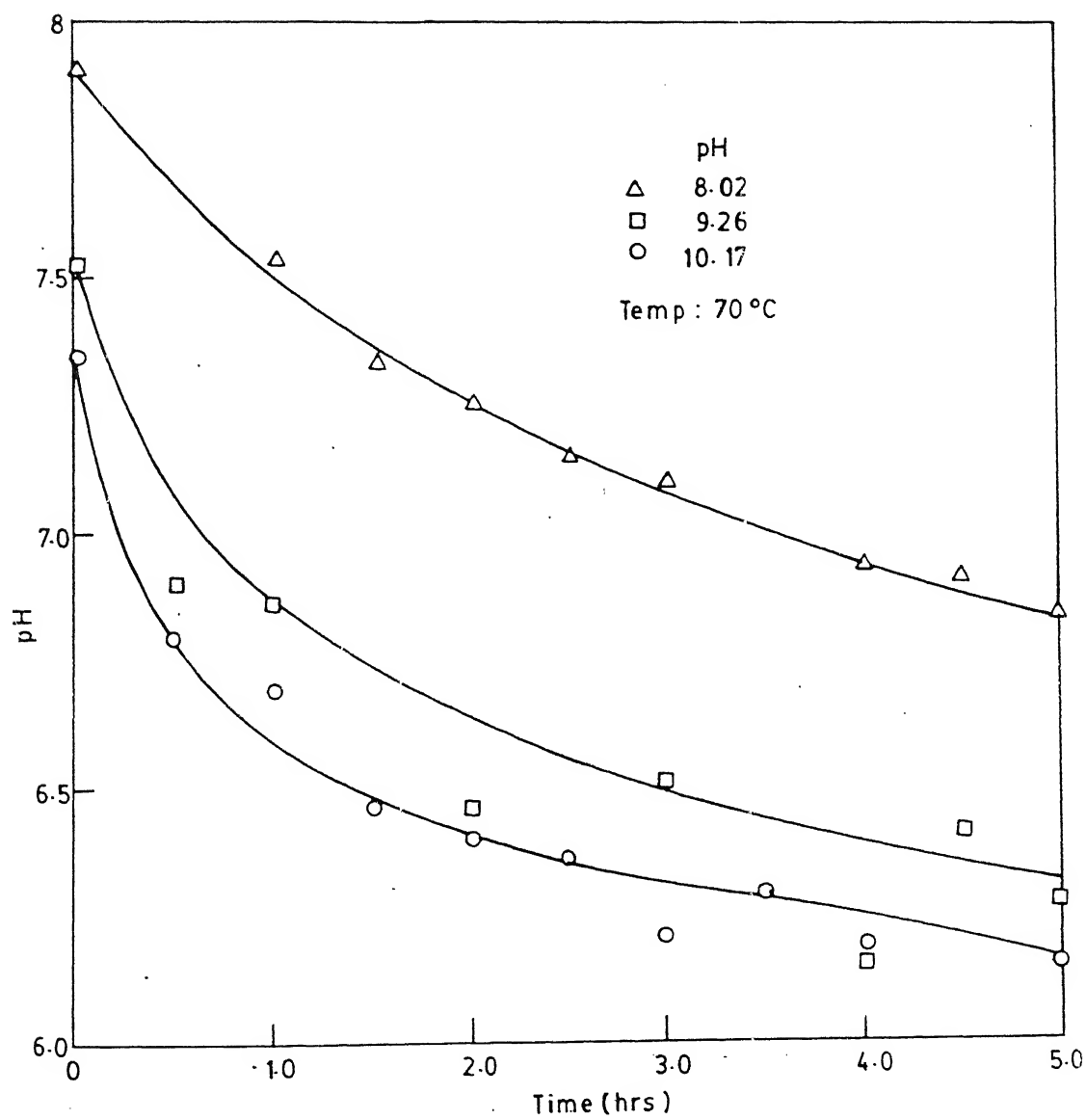
FIG. 12 EFFECT OF INITIAL pH OF THE COMPLEX: VARIATION OF pH
WITH TIME (HRS)
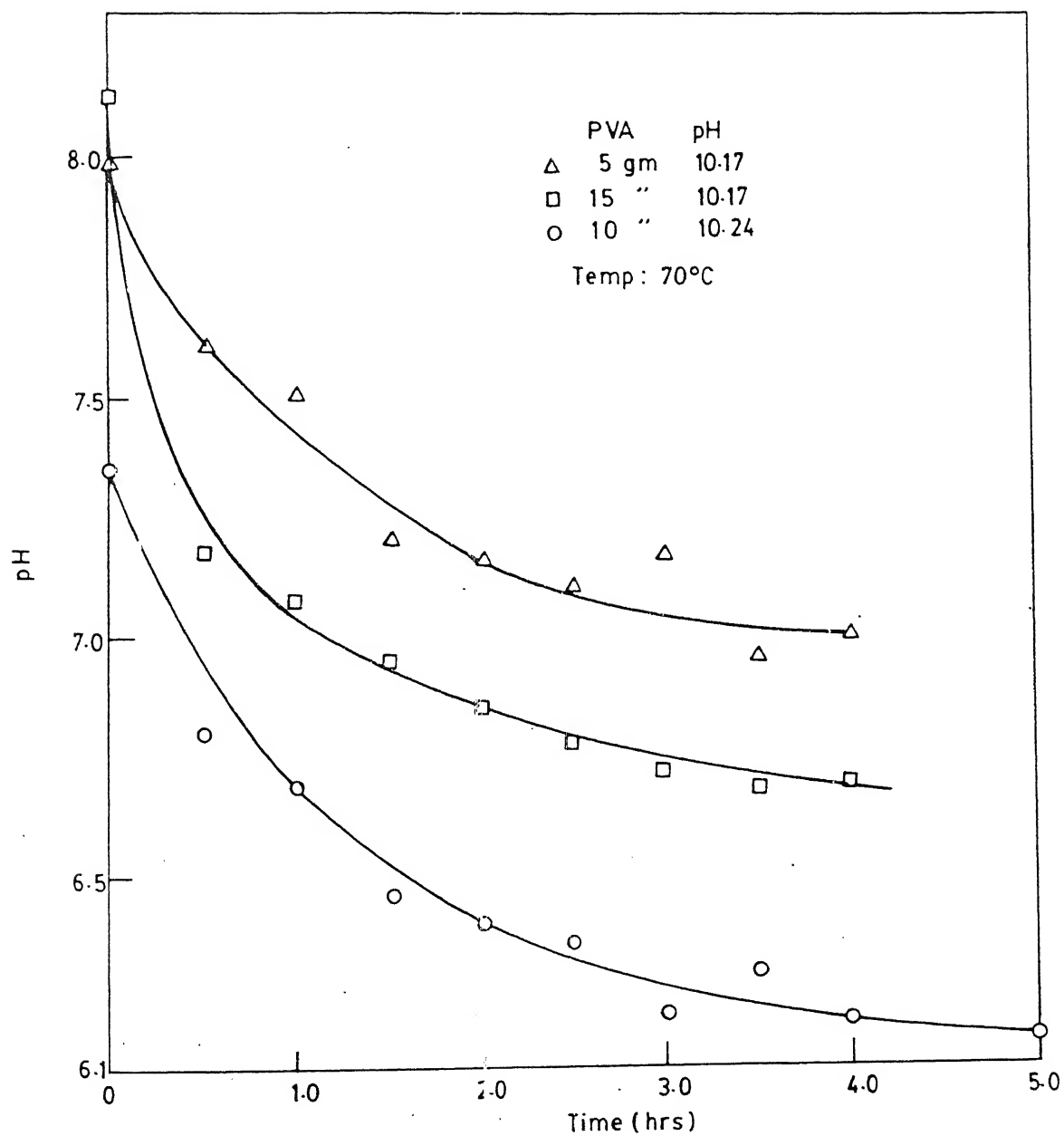
FIG. 13   EFFECT OF PVA CONCENTRATION :   VARIATION OF pH WITH TIME(HRS)
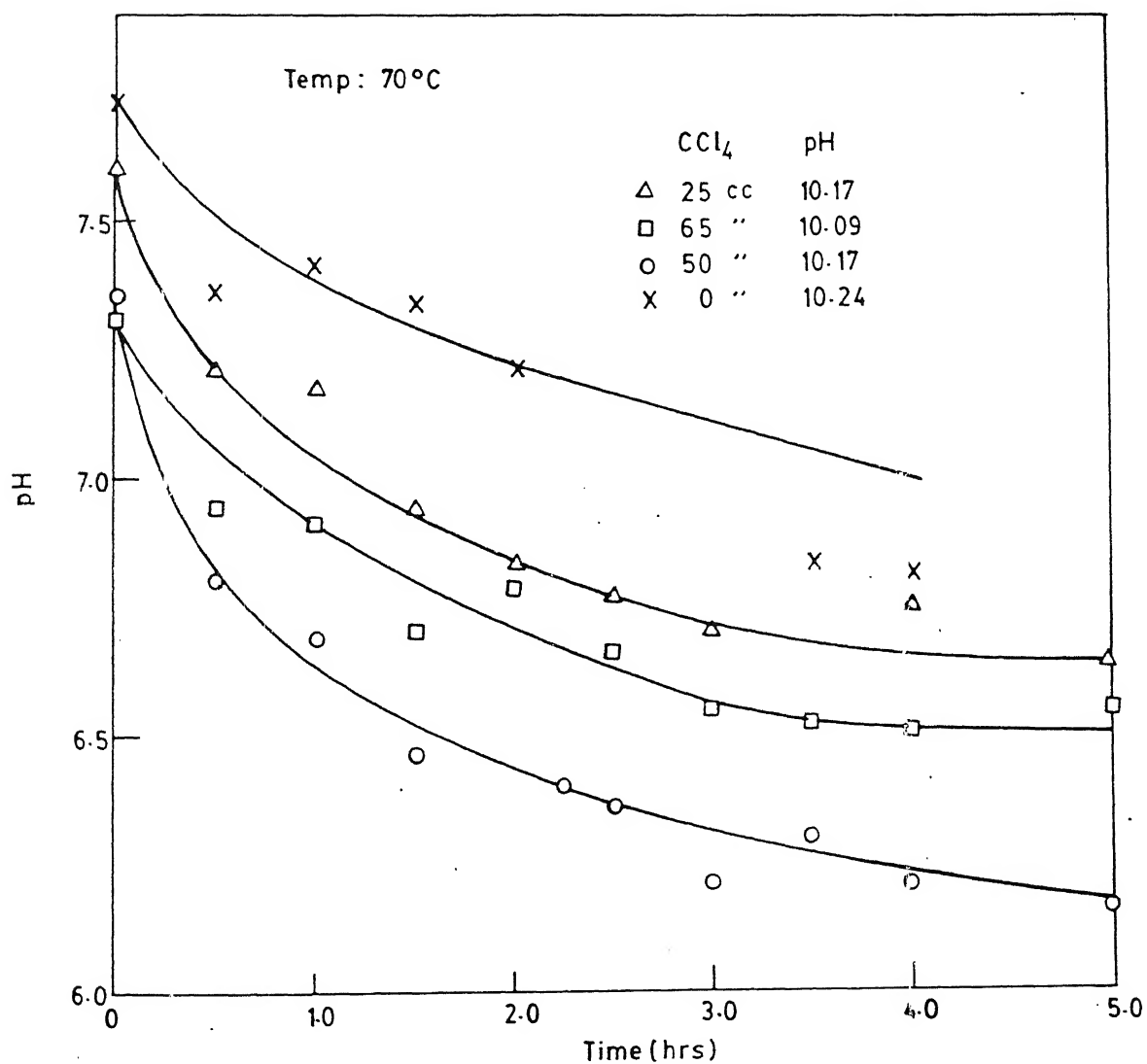
FIG. 14 EFFECT OF AMOUNT OF CCl₄ :   VARIATION OF pH WITH TIME(HRS)
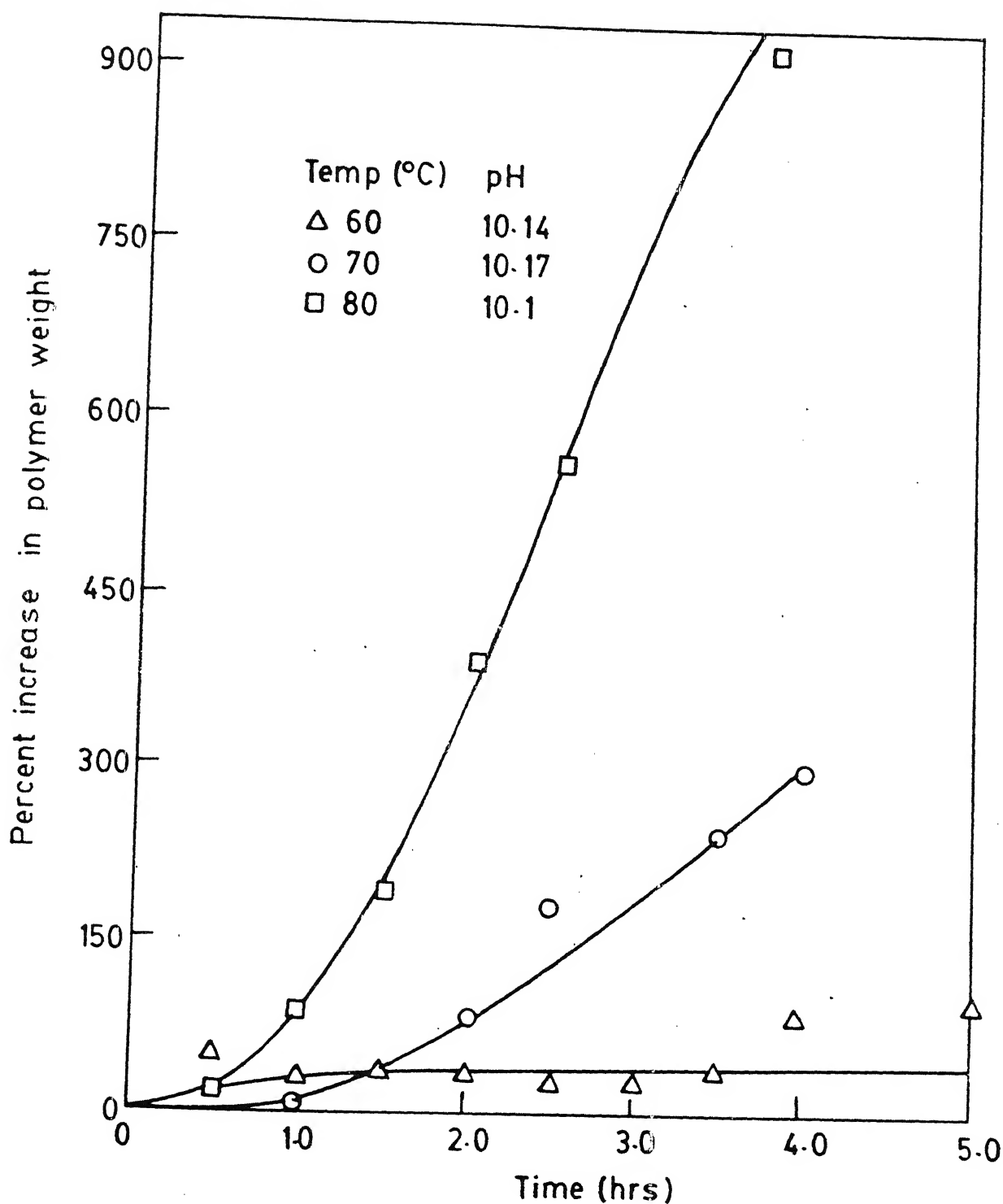
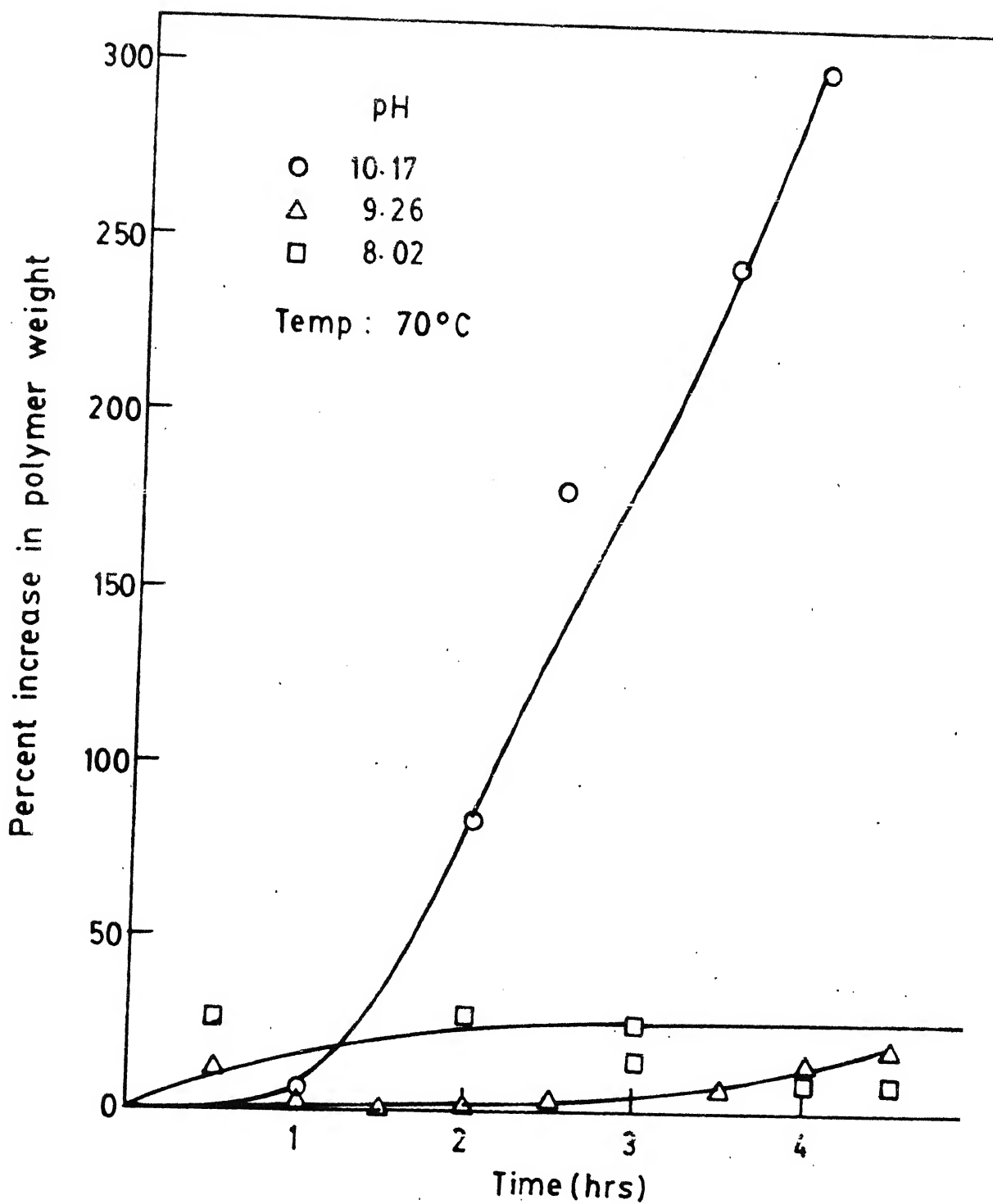FIG. 15   EFFECT OF TEMPERATURE:PERCENT INCREASE
IN POLYMER WEIGHT VS. TIME (HRS)

FIG. 16   EFFECT OF THE INITIAL pH OF THE COMPLEX:
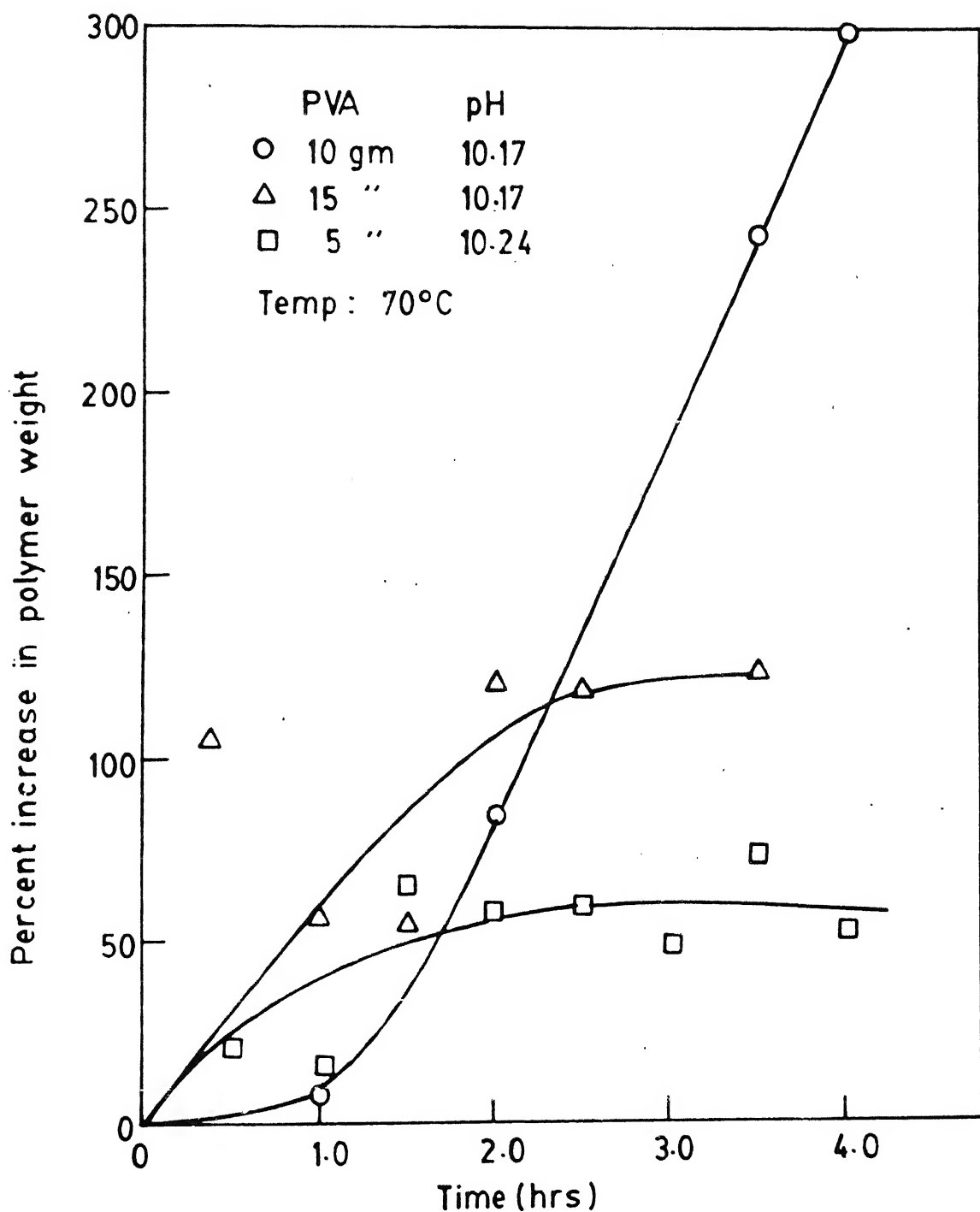PERCENT INCREASE IN POLYMER WEIGHT VS T

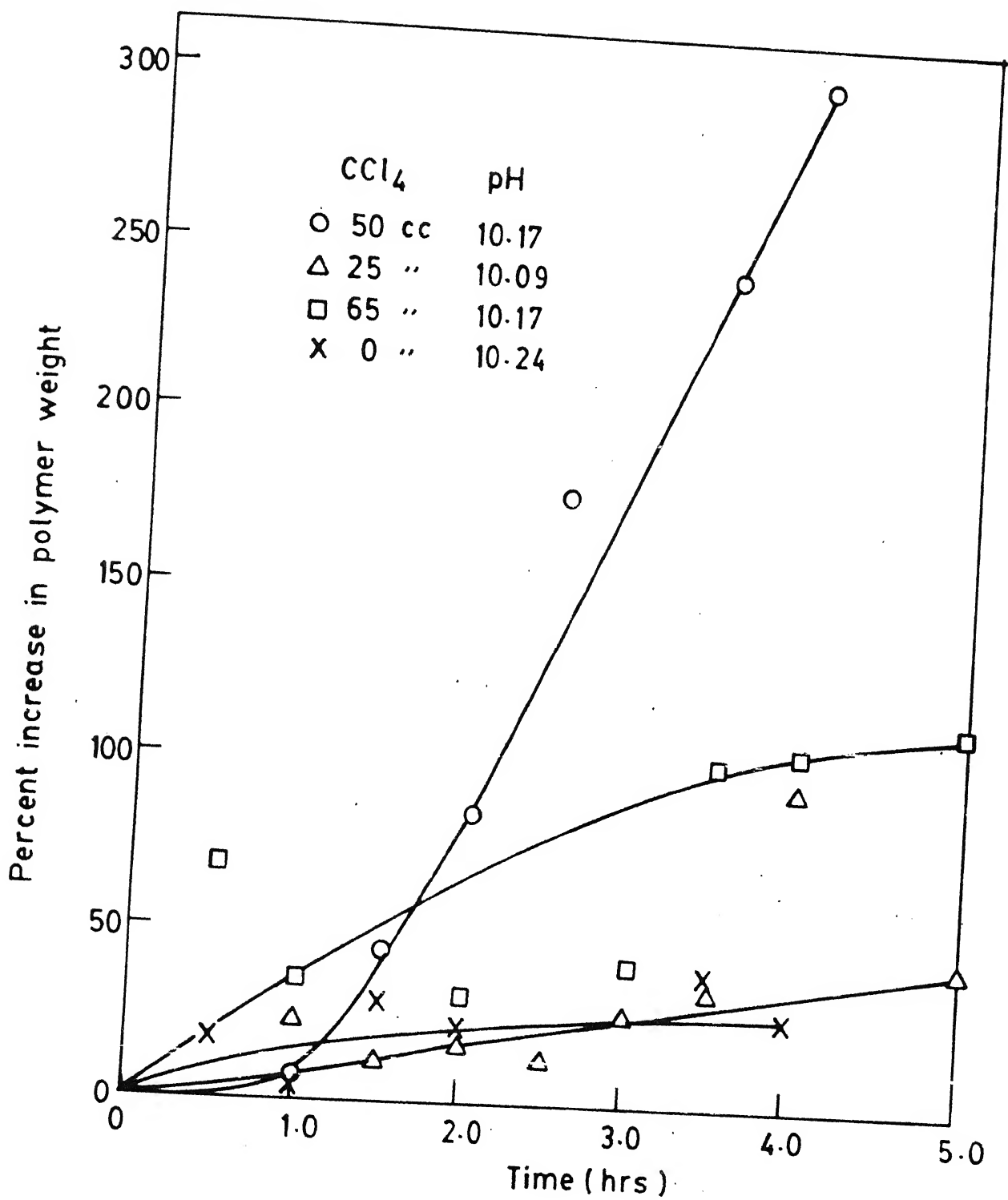FIG. 17 EFFECT OF PVA CONCENTRATION:PERCENT INCREA
IN POLYMER WEIGHT VS TIME (HRS)

FIG. 18 EFFECT OF AMOUNT OF CCl$_4$:   PERCENT INCRE
IN POLYMER WEIGHT VS TIME (HRS)

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